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ESTIMATION OF FREE FORMALDEHYDE IN RESIN-TREATED COTTON FABRICS

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Aldehydes and ketones react with hydroxylamine hydrochloride to form oximes, liberating hydrogen chloride in the process. The relationship is stoichiometric and the liberated hydrogen chloride may be calculated as aldehyde or ketone as the case may be. The procedure described involves ethanol-water extraction of the fabric, potentiometric neutralization of the extract to pH 7.00, reaction with hydroxylamine hydrochloride, potentiometric neutralization to pH 3.40, and calculation of the results as free formaldehyde.

INTRODUCTION

THERMOSETTING resins, so extensively used in imparting wrinkle resistance, dimensional stability, etc, to cellulosic fabrics, generally contain free formaldehyde. This is picked up by the cloth and persists to some extent even after curing. The finished materials are often shipped to the garment maker, etc, without the benefit of scouring or washing. The free formaldehyde can therefore present a problem to the cloth cutter, the retail store, etc, particularly during warm and humid weather, provided it is present in sufficient quantities. A reliable method for estimating free formaldehyde in cellulosic fabrics is therefore a necessity for any finishing mill.

Heretofore, the Tootal Broadhurst Lee method *(1)* has been the accepted technique for estimating free formaldehyde in resin-treated cotton fabrics. This involves water extraction of the sample, treatment of an aliquot of this extract with Schiff's Reagent and hydrochloric acid, simultaneously treating aliquots of a known concentration of formaldehyde in the same manner, then heating at 80° C for five minutes, and finally making a colorimetric comparison between the extract and the standards. The results are generally low probably due to incomplete extraction of the formaldehyde since overnight extractions of samples give values as much as 100% greater than those obtained with use of the standard method. Mercurimetric methods *(2)* may also be employed but they do not give good precision. The procedure which follows has been adapted from the method of Haslam and Soppet for determining free formaldehyde in phenol-formaldehyde syrups. It is based upon the reaction of ketones and aldehydes with hydroxylamine hydrochloride to liberate hydrogen chloride. The relationship is stoichiometric and the liberated hydrogen chloride can be titrated with standard base and the results interpreted as free formaldehyde.

PROCEDURE

Wet two 2-gram samples of cloth in 250-ml beakers with 25-ml aliquots of 95% ethanol. Add 50 ml of water, cover with watch glasses, and let stand for twenty minutes with occasional stirring. Squeeze by hand and re-extract two times with 25-ml aliquots of water, squeezing each time by hand after five minutes of extraction. Combine extracts and neutralize to pH 7.0 potentiometrically. Add two grams of hydroxylamine hydrochloride, stir until the latter has dissolved, let stand for 30 minutes, then titrate to pH 3.40 potentiometrically using N/10 NaOH. Run duplicate blanks using only the reagents.

Calculation:

$$\text{Formaldehyde, ppm} = \frac{T_1 - T_2 \times N \times 0.03 \times 10^6}{\text{Wt of sample}}$$

Where T_1 is the sample titration
T_2 is the blank titration
N is the normality of the NaOH

RESULTS AND DISCUSSION

Generally speaking the blank titrations are in the range of 0.4 ml of N/10 NaOH while the net titers amount to approximately 0.3 - 0.5 ml. An accurate pH meter is therefore necessary. More dilute NaOH solution may be employed to increase the titers. However, we have found the N/10 NaOH to be entirely satisfactory.

Other alcohols may be employed in the initial extraction. In tests with ethanol and isopropanol on known concentrations of formaldehyde, the results obtained with isopropanol were always low in a range of concentrations between 200 and 3000 ppm. Ethanol gave close to the theoretical values and is therefore the solvent of choice.

When adjacent samples of resin-treated cloth were tested using the Tootal Broadhurst Lee method, it was found that a progressive increase of the extraction time progressively increased the value for the formaldehyde reporting such that the figure for nineteen hours could be as much as fifty to one hundred percent greater than that for the twenty minutes originally recommended. This would seem to indicate incomplete extraction when the shorter time interval is employed. Further, the Tootal Broadhurst Lee method gives poor precision, values for duplicate samples sometimes being at variance as much as fifty percent.

An adaptation of the mercurimetric method of Pfeil and Guenther failed to give precise results. Also the inability to produce a well defined end point lessens the accuracy of that method considerably.

The hydroxylamine hydrochloride procedure as outlined gives excellent precision, reports known concentrations of

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CONTROL OF THE VAT-DYEING PROCESS*

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The account of the establishment of a Russian laboratory method of dyeing control, from a short abstract in *Chemical Abstracts*, seemed to offer interesting possibilities. This led Dr Barabash to translate this article, which was edited by P J Wood, with the assistance of George L Royer and Fred Fordemwalt of American Cyanamid Co, who supplied the additional references *(10-13)* which follow the Russian references at the end of this article.

TWO basic methods of vat dyeing are: 1) dyeing in leuco solutions with the subsequent oxidation of the leuco compound, which is sorbed by the fiber, and 2) two-phase or suspension dyeing by the method of M A Ilinskii, which consists of impregnating the fiber with a highly dispersed nonsubstantive dye, transforming it into the substantive form, and finally fixing it on the fiber.

The following variables must be controlled when the first method is used: the amount of dye on the fiber, alkali and hydrosulfite content in the bath; concentration of dye in the leucoform; (it is also desirable to know the amount of unreduced dye); concentration of assistants in oxidizing and scouring baths.

When the second method is used, the constituents of each bath must be determined separately: the amounts of dye and of assistants in the suspension bath, the amounts of alkali, or hydrosulfite and washed-off dye in the developing bath, amounts of oxidizing agent, of alkaline-soap solution, etc in the washer. The amount of dye on the fiber must also be known.

The technological parameters of vat dyeing, such as temperature, volume of liquors used, reaction time, steaming, etc, can be automatically controlled in present-day equipment.

A set of laboratory control methods has been investigated and developed, which is described in this paper. A distinct characteristic is the use of physico-chemical processes in conjunction with appropriate apparatus.

More specifically, the controls of alkali, hydrosulfite and dye concentrations in suspension and in the leuco baths, and the amount of dye on the fiber have been studied.

A study of alkali and hydrosulfite concentrations in the leuco solutions will determine (at a given temperature) the existence of the leuco form and its solubility. In the reducing baths it will determine reduction rates and the fixation rate of dye suspension on the fiber. At this time two oxidation-reduction systems originate simultaneously, that of the dye and that of the hydrosulfite. The first is a reversible system, the second is practically irreversible.

$$S_2O_4^{=} + 4OH^- - 2e \rightarrow 2SO_3^{=} + 2H_2O$$

The oxidation-reduction system obviously can be controlled by control of the corresponding potentials. But calculation and experience have shown that the control is only qualitative since the potential of the corresponding indicator electrode is determined by two processes: the concentration and reaction rates. It should be noted that the pH of the medium, which is changing during dyeing and aging, will also substantially affect the potential. Oxidation-reduction potentials in alkaline solutions of hydrosulfite and in leuco solutions of vat dyes were determined using graphite, platinum and gold indicator electrodes and a calomel electrode for reference. An electronic potentiometer previously described *(1)* was used for these measurements.

Figure 1 shows the results of measurements of oxidation-reduction potentials in alkaline solutions of hydrosulfite (0.1 n Na_2CO_3, pH = 10.8) at three concentrations (3, 1 and 0.1 g/l; curves 1, 2 and 3, respectively).

Two parallel platinum electrodes were used for these measurements, the solutions remaining under atmospheric conditions without stirring, with the exception of a one-minute stirring after the addition of hydrosulfite. Fast changes of the potential occur in the first few minutes, after which an equilibrium value is slowly reached. Large difference in absolute values of oxidation-reduction potential is observed only for initial low concentrations of hydrosulfite. With an excess of hydrosulfite the potential assymptotically approaches the average equilibrium value. On the contrary, decomposition (oxidation) of hydrosulfite (curve 3) is characterized by a distinct change in the potential.

Similar phenomena are observed in neutral solutions (buffer pH = 7.1).

Introduction of leuco solution markedly increases the oxidation-reduction potential. Thus, in the leuco solution of Vat Blue K (0.3 g/l) the potential (with gold electrode) is 960 mv; without the dye it is 880 mv. Figure 2 shows the changes of the potential (gold electrode) of a leuco solution (Vat Blue K) during 1 hour under fixed conditions.

Similar results were obtained with other vat dyes, for Vat Bright Green C, for example.

Data obtained show that the value of oxidation-reduction potential or pH cannot be used to measure hydrosulfite concentration in leuco solutions or in reducing baths. This value, however, can be a good indicator of the excess of the reducing material in continuous dyeing when a continuous control method is organized.[1]

For laboratory determination of hydrosulfite concentration a series of methods has been recommended, one of which was reported in GOST 246-41.[2] But not a single one of these methods can be used for analysis of strongly alkaline industrial liquors containing intensely colored leuco compounds. For this purpose we offered, developed and used a potentiometric titration with potassium ferricyanide (platinum indicator electrode) and a colorimetric method *(3)*.

It must be noted that the alkali-hydrosulfite liquor is constantly changing, especially in the air. Special measures to preserve this solution for analysis therefore must be made. Analytical data of hydrosulfite and alkali content can be related only to a given time interval.

NaOH content in reducing baths and in leuco solutions cannot be determined by an ordinary titration with an indicator, since the latter will be decomposed by hydrosulfite. For this purpose we developed electrometric methods using a glass electrode (potentiometric titration) and conductometry (measure of electric conductivity).

A "working" alkali-hydrosulfite bath some time after its preparation will contain

$S_2O_4^{=}$, $SO_3^{=}$, Na^+, OH^-, $CO_3^{=}$, $S_2O_3^{=}$

ions and, possibly, small amounts of other

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* Translated from the Russian; *Tekstilnaya Promyshlennost* 14, No. 2, 20-4 (1954).

[1] 1½ years after this work had been reported in a meeting of the Central Institute of Cotton Industry, an advertising report on a similar study carried out in USA appeared *(2)*.

[2] GOS = State; T = probably stands for technology. (E B)

salts of polythioacids. Sulfide ions were not found. In leuco solutions, in addition, the ions of leuco compounds are present in various forms. These are determined by physico-chemical properties of the dye itself, and the colloidal dispersions of the dye. When such a complex mixture is titrated conductometrically with a solution of a mineral acid, in accordance with the chemical activity of the constituents, the hydroxyl ions will be the first to react, then the remaining ions, in order of their activity and electrolytic mobility. The conductiometric chart gives a clear idea of the presence and amount of a most important constituent in the dyeing operation — sodium hydroxide.

In Figures 3 and 4 curves of conductiometric titration are given; for alkaline-hydrosulfite solution, see Figure 3; for the leuco solution, see Figure 4. Each of the curves is characterized by two breaks, the first corresponding to the completion of reaction with NaOH; the second, to the completion of reaction with other constituents. This method has been shown to be reproducible. The accuracy of determination of NaOH is the same as in an ordinary volumetric determination, ± 0.1 ml of the titrating solution. The presence of leuco compounds does not interfere with conductiometric determination of alkali. *The following fact should be pointed out:* the alkali, which is usually stoichiometrically related to the leuco compound, and the hydrosulfite, necessary to the formation of the latter, according to the electrometric determinations, are both as active as the remaining part of these materials which is in solution. This fact may be used for evaluation of the physico-chemical properties of leuco compounds.

In considering the curves of Figures 3 and 4 one should note the difference in the values measured by the ordinates, ie, resistance in Figure 3, conductivity in Figure 4. In Figure 3 the family of curves represents the decrease in NaOH with aging of solution, the growth of the middle section (Na_2CO_3, $NaHSO_3$), the decrease of stability during storage. Curves 1 and 2 characterize the resistance after 15 minutes; curves 3 and 4, after 4 hours; curve 5, resistance of NaOH. Curves of Figure 4 characterize the formation of "leuco acid" of indigo (violet color) during titration of leuco solutions in the presence of a protective colloid (sulfite liquor).

Any modern apparatus for conductometric titration may be used for this purpose. Those with galvanometers and other visual indicators are preferred to older types with telephones and buzzers. The technique of conductometric titration is described in a work sheet *(9)*.

A method for colorimetric determination of the concentration of vat dyes in leuco solutions proposed by one of the authors in 1931-32 *(4)* replaced other more complicated methods. Colorimetric determination of dye suspension has been reported earlier *(5)*. For analysis of leuco solutions we used two methods: stabilizing (deactivating) diluted leuco solutions with protective colloids *(9)*, and obtaining hydrosols by oxidizing diluted leuco solutions with H_2O_2, in small excess, in the presence of protective colloids.

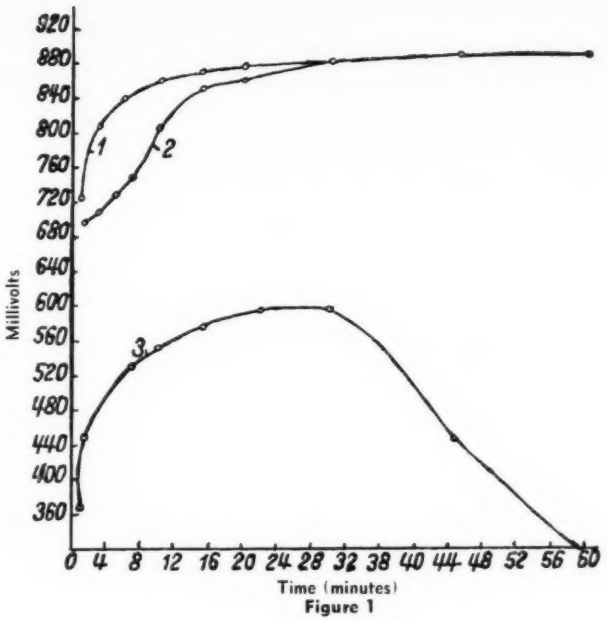

Figure 1

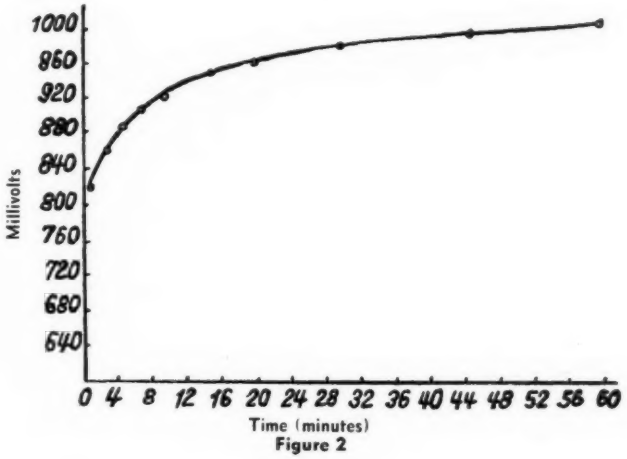

Figure 2

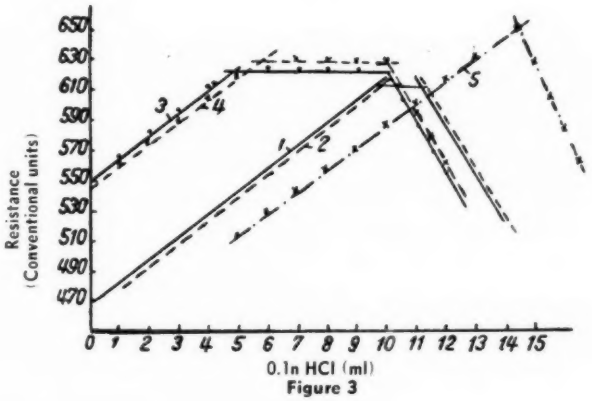

Figure 3

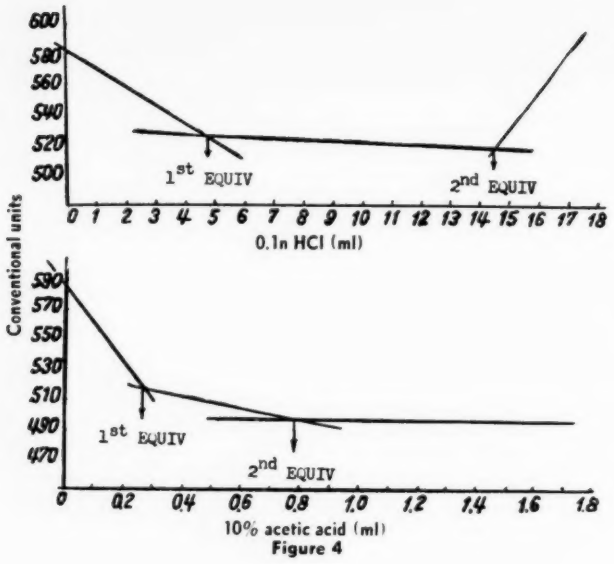

Figure 4

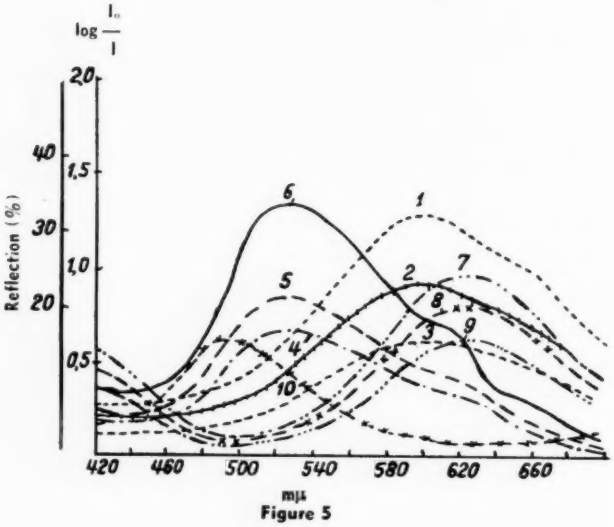

Figure 5

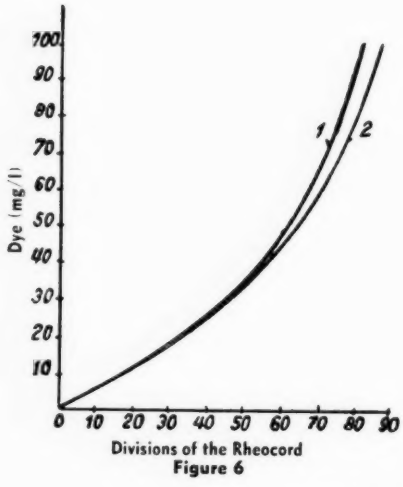

Figure 6

A common objection to the spectrophotometric and colorimetric analysis of colloidal sols of dyes is that an intensive light diffraction must take place in colloidal sols.

Multiple experiments carried out by the authors have shown that, under experimental conditions accepted for spectrophotometric and colorimetric analyses, the light diffraction is negligible and practically does not affect the results obtained. Beer's law concerning the relationship between concentration and the magnitude of adsorption, is followed in all cases of colloidal sols of dyes. Hence the regular spectrophotometric and colorimetric analysis is completely suitable for colloidal sols of vat dyes.

A method is discussed below which is most suitable for plant laboratory preparation of sols of oxidized leuco solutions and their colorimetry.

With regard to the objective of the analysis, a material is prepared for comparison and evaluation of obtained data. For analysis of continuous baths (running control), the original bath might serve as a standard. In order to obtain comparable results it is expedient to prepare a calibrated chart of results obtained in a photoelectrical colorimeter of sols of known concentration. To a sample of dye, stirred into a smooth paste with a small amount of alcohol, are added alkali, hot water and hydrosulfite. After careful dissolving and cooling to room temperature, a known volume of the leuco solution is pipetted into water containing H_2O_2 and the protective colloid. As protective colloids, gelatin, OP-10 or Emulphor (condensation product of ethylene oxide and dodecyl alcohol) are used; the latter provides a greater stability of the sols.

A sol from the powder of Vat Blue K is prepared as follows:

0.1 g of dye plus alcohol plus 0.3 ml NaOH (40%) is stirred into a paste with 50 ml of H_2O at 55°C; 0.2 g of $Na_2S_2O_4$ is added. 15 minutes later, after the volume is adjusted to 100 ml, the reduction is completed. 5 ml of this leuco solution is pipetted, with the top of the pipette below water surface, into 50 ml of H_2O containing 4 g/l of Emulphor (30%), and is oxidized with 0.5 ml of H_2O_2 (3%). During sol formation, the oxidized leuco compound is converted into the original pigment, highly dispersed.

Naturally, in analysis of working plant bath, the preparation of leuco solutions is omitted since aliquots are taken out of the bath. Complete solution of the dye is a necessary requirement, as only the dissolved dye is transformed into a sol.

Depending on individual properties of different dyes and on the amounts of protective colloid, sols with 20-100 g/l concentration may be obtained. In subsequent unlimited dilution with water the

aggregation stability of the sols is preserved. The color of the sol and the corresponding value of its specific absorption remain unchanged for a few hours, which is quite sufficient for all analytical procedures. Formation rates and the length of preservation of stable sols vary for different dyes. For instance, for the sol obtained from the Bright Green G 48 hrs after preparation, an increase in the absorption in the red part of the spectrum and a decrease in the blue part were observed. The total decrease, with respect to the total area under the curve lying between 400-700 mμ, was 2.4%. Under identical conditions of preparation and storage of control sols and sols which were used for making the charts in colorimetry (or for the standard solution in spectrophotometry), the error does not exceed ± 2%, which is quite satisfactory.

In Figure 5 some of the spectrophotographs obtained for hydrosols of vat dyes purified by recrystallization from organic solvents are given. Curves 1, 2 and 3 are for Vat Blue O in concentrations of 80, 60 and 40 mg/l, respectively. Curves 5, 6 and 7 are for Vat Bright Violet K in concentrations of 23.3, 35 and 46.6 mg/l. Curves 7, 8 and 9 are for Bright Green C in concentrations of 25, 20 and 15 mg/l. Curve 10 is for Vat Bright Green C on cotton fabric. The right ordinate applies for curves 1-9, the left (% reflection) is for curve 10. With data from curves in Figure 4, charts can be plotted showing the relationship between the extinction coefficient and the concentration (log Io/I — C). Their straight line relationship shows that there is a regular relationship here between the absorption value and the concentration and that the colorimetric analysis is quite satisfactory. The pattern of spectrophotometric curves shows that the most suitable monochromatic colorimetry, using filters corresponding to the absorption bands of solutions, is: for Vat Blue O, in the region of 590 mμ; for Bright Violet K, 540 mμ; for Bright Green C, 620-630 mμ.

A chart for hydrosols of Vat Bright Green G obtained on the photoelectrical colorimeter is shown in Figure 6 (curve 1); for comparison, the aqueous suspension of the same dye is shown in curve 2. These charts were obtained by successive colorimetric determinations of a series of hydrosols (and suspensions) of a known dye content. With this chart it is easy to determine the concentration of the analyzed hydrosol by noting its absorption in the photoelectric colorimeter by noting the Reochord measurements.

When a mixture of two dyes is used, two possibilities may arise. Both constituents of the mixture are adsorbed by the fabric at the same rate; this permits the use of the chart plotted for the mixture. If, however, the dyes are adsorbed by the fabric at different rates and show markedly different absorption spectra, then two charts must be prepared, one for each constituent, using corresponding filters as described above.

A number of methods can be used for determination of vat dyes on cellulose fiber, such as cellosolve extraction *(7)*, organic liophyllic solvent extraction *(8)*, and others. Repeated verifications showed that, from a practical point of view, a desirable method is that of colorimetry of sulfate sols, which was proposed by A I Sokolov. These sols are obtained by dissolving a sample of the dyed material in a small amount of H_2SO_4 and pouring this solution into cold water containing the protective colloid. As in the case of preparation of sols by oxidation of leuco solutions, the colorimetric advantages of hydrosulfosols are used in this method as compared to the solutions of H_2SO_4, such as greater brightness and greater value of specific adsorption. It is also possible to work in considerably diluted H_2SO_4. The quantitative determination of the amount of the dye deposited on the yarn is obtained by comparison with sols formed by the same method from a weighed sample of powdered dye.

In order to obtain hydrosulfosols, a small (0.1-0.2-g) amount of accurately weighed, dyed fabric is cut in small pieces and dissolved in 5-10 ml H_2SO_4 (CP grade, sp gr 1.84) at room temperature with occasional stirring for 1 hour. This solution is then diluted in a volumetric flask with distilled water containing a protective colloid (for instance, 4g of the paste OP-10). A calibrated chart is obtained by preparing sulfosols of powdered dye; 50 mg of the dye is dissolved at room temperature in 25 ml of H_2SO_4 (sp gr 1.84) and the solution is poured into 900 ml of distilled water containing 4 g/l OP-10 (or Emulphor). It is cooled by immersing in cold water. The volume is brought to one liter in a volumetric flask, and by diluting portions of this solution, 6-8 solutions of various concentrations are obtained for use in making the chart.

When partially neutralized leuco compounds (leuco acid method) are used, the pH of the solutions must be controlled, since it determines their stability and activity. Method of the plant control of pH is discussed in an earlier study *(1)*.

In addition to the problems discussed here, a number of others of more general interest arise in the control of processes of vat dying, eg, control of the squeezing of the fabric, determination of concentrations of assistants, degree of rinsing of the fabric, etc.

CONCLUSIONS

1) A laboratory control of vat-dyeing processes for one and two-phase methods is proposed. It is based on the use of the photoelectrical colorimeter, an apparatus for determination of electro-conductivity and a lamp pH meter.

2) In conjunction with an automatic control and regulation of parameters of the technological process on a suitable apparatus (temperature, liquid level, speed, squeezing, etc), the proposed method enables one to direct the process and rationally use dyes and assistants.

REFERENCES

(1) Russian source.

(2) Textilber 33, No. 9, 862 (1952).

(3) Bielenkii, L E and Kazankaya, M E, *Tekstil Prom*, No. 6, 35 (1952).

(4, 5) Russian sources.

(6) Tekstil Prom, No. 12 (1947).

(7, 8 and 9) Russian sources.

ADDITIONAL REFERENCES

(10) Controlled Vat Dyeing. Zimmerman, C L, Mecco, J M, Fordemwalt, F and Cooke, T F, "I—The Stabilization of Vat Dyes at Elevated Temperatures"; Royer, G L, "II—Instrumental and Analytical Measurement"; Lineken, E E, Grand, S and Fordemwalt, F, "III—Leuco Potentials", *Am Dyestuff Reptr* 41, No. 20, P597-610 (1952).

(11) Marnon, D E, "The Marhen Process", *ibid* 41, No. 10, P292 (1952).

(12) Marshall, W J and Peters, R H, "The Reduction of Vat Dyes in Printing Paste", *J Soc Dyers Colourists* 69, No. 13, 583 (1953).

(13) Hensel, O, "Reduction-Oxidation Potential of Vat Dyestuffs", *Textilber* 35, No. 5, 513 (1954).

Estimation of Free Formaldehyde in Resin-treated Cotton Fabrics—

(Concluded from page 53)

formaldehyde quantitatively, is quite easy to carry out, and therefore appears to be a superior method for estimating free formaldehyde in resin-finished cotton fabrics.

SUMMARY

A simple method for estimating free formaldehyde in resin-treated cotton fabrics has been presented. The technique involves ethanol-water extraction of the fabric followed by potentiometric neutralization of the extract to pH 7.0, treatment with hydroxylamine hydrochloride, finally neutralizing to pH 3.40 potentiometrically with N/10 NaOH, and calculating the results obtained.

REFERENCES

(1) "Tebilized" Plan—USA, Memorandum of Tests, Tootal Broadhurst Lee Co, Ltd, Manchester, January 1952.

(2) Pfeil, E, and Guenther, S, Z *anal Chem* 134, 332 (1952).

(3) Haslam, J, and Soppet, W W, *J Appl Chem* (London) 3, 328 (1953).

THEORY AND PRACTICE OF ENZYMATIC DESIZING*

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INTRODUCTION

IN THE period between the two World Wars one received the impression that development in the field of enzymatic desizing had come to an end. The malt diastases, the pancreatic ferments and the bacterial amylases were known, and each of them had an apparently well-defined area of application depending upon its production, price and properties. No necessity for creating new amylase types seemed to exist; therefore no one was concerned with the chemistry of desizing. The fact that these products were capable of removing starch from fabrics sufficed. It was only in the United States that these things were questioned. Higher labor costs created the necessity for faster desizing and the resulting continuous processes gradually brought the bacterial amylases to the fore. In Europe the same development took place after World War II, in addition to the fact that, in Germany, the bacterial amylases could be prepared from waste material readily available. It is no wonder that, today, all the important amylase manufacturers pay a lot more attention to the heat-resistant bacterial amylases. New desizing processes have become of interest. Then too, research has been conducted towards amplifying the process of desizing in order to reduce the cost of this operation. The following discussion gives a brief resume of this development.

INVESTIGATION OF ENZYMATIC DESIZING

The problems in the investigation of enzymatic desizing are known. The latest works, in which the difficult solubility of dextrine is referred to as a characteristic of the conversion of dissolved starch, have indeed made progress, but have certainly not reached the heart of the matter. The necessity of carrying out the enzymatic desizing on solid starch precipitated from a solution has become increasingly clearer. These ideas are certainly not new, but up to now they have not been confirmed, and we are still faced with the problem of obtaining sufficient quantities of the type of starch necessary for extensive experiments. The question of carrying out the conversion of starch hinges, therefore, upon the possibility of obtaining larger quantities of undissolved starch by laboratory methods. A brief resume of the procedure used follows[1]:

40 g of potato starch (or a starch briefly pretreated with acid as in a technical sizing process) is heated to the boil in 500 cc of water while being rapidly agitated. It is kept at this temperature for 15 minutes. A neutralizing solution of 200 g of ammonium sulfate in 500 cc of water is added. The mixture is boiled 5 minutes longer and quickly cooled to 30°C. At this point a mixture of 600 cc of methanol and 1200 cc of acetone are added, making sure that the mixture remains cool. The mixture of ammonium sulfate and starch which separates out is filtered off by suction and dried at about 40°C. The ground product is then stirred with 30% methanol and filtered by suction and washed with 30-40% methanol until it is free of ammonium sulfate. It is dried at 40-50°C. *Yield*: 36.5 g with a moisture content of 10%.

It has been shown that the precipitates so obtained are not completely uniform but little difference is apparent in the rate of conversion. At times we mixed together a large number of batches in order to obtain a homogeneous material.

Because they were obtained by boiling starch in water, these starches were essentially different in their behavior both from natural starch and from dissolved starch, which were used in investigations made heretofore. From our experiments it seems quite plausible to assume that this starch very nearly approximates a starch film. Whereas in the natural starch grains amylopectin and amylose lie tightly packed in a regular order next to each other so that they cannot be attacked by enzymes, those of the precipitated starch have no definite pattern. In a starch film, also, it can be assumed that the pattern of the amylose and the amylopectin molecules is irregular, especially if the starch solution is dried very rapidly. Because of the disorientation, both starch molecules are surrounded by a solvation envelope, ie, they can swell, the degree of swelling being dependent upon the temperature. There are certain differences between the precipitated starch, which was the principal one used in our experiments, and a starch film. The latter exhibits a closed, and what is more important, an essentially smaller surface than the former. Consequently the precipitated starch possesses greater water solubility and a higher rate of reaction while at the same time having the same conversion end point. It was therefore important to supplement the experiments on precipitated starch with some on starch films. When compared with dissolved starch, the starch obtained from solution by precipitation or drying showed considerable deviation. It does not require the addition of as large a quantity of enzyme as is used commercially at temperatures below 50°C to cause complete conversion to soluble products.

In investigating enzymatic conversion of precipitated starch we used the following procedure, which, unless stated to the contrary, was retained in subsequent investigations:

3.2 g of the precipitated and dried starch to be tested was stirred in 100 cc of water and heated to the reaction temperature. The enzyme, dissolved in 20 cc of water, was added, the pH adjusted and the mixture held at the reaction temperature for the desired time. If the desired time amounted to one hour the mixture was stirred constantly. If the mixture was to stand over night, it was stirred for two hours only and allowed to stand without stirring at constant temperature for the remaining time. The insoluble portion was centrifuged off, stirred up with methanol, vacuum filtered, rewashed with methanol and dried.

From this procedure it was found that the precipitated starch being tested had a grain structure of the following composition:

Particle size	*(%)*
Over 0.4 mm dia	0.41
0.3-0.4 mm dia	0.58
0.2-0.3 mm dia	18.60
0.1-0.2 mm dia	63.00
Under 0.1 mm dia	17.50

From this starch (I) an exceptionally fine starch (II) was separated by passing it through a Mueller gauze. Overnight treatment with 0.1 g of bacterial amylase containing 0.4 AU/g at 40 and 50°C gave the following residues[2]:

* Translated from the German; *Melliand Textilberichte* 35, No. 7, 762 (1954).

[1] This experiment can be carried out using the commercial so-called swollen starch obtained from a starch solution by drum drying it and then grinding it. One must take into account that the previous history is not known and the length of time the material was in storage is not known.

[2] AU/g = Amylase units per gram (*1*).

	Temp (°C)	Residue (%)
Starch I	40	13.9
	50	7.3
Starch II	40	12.9
	50	7.1

Within these limits there were no important differences with either shorter or longer periods of reaction. The differences in the degree of conversion between larger and smaller particles were also not appreciable so that conclusions could be drawn regarding the desizing procedure.

Disregarding the concentration of the enzyme solution used for desizing, the desizing temperature and the length of time of desizing are decisive factors in a normal desizing. We investigated their influence by our methods.

The question of the effect of temperature was especially interesting because one group of enzymes (the malt amylases) had evidenced anomalies using earlier experimental methods.

In accordance with the above-described method, 3.2 g of starch and 120 cc of water in toto plus the following amounts of enzymes were used for these tests. A bacterial amylase containing 0.4 AU/g, a pancreatic product containing 1.8 AU/g and a malt amylase containing 1.05 AU/g were used. The reactions with the pancreatic and bacterial amylases were carried out at a pH of 6.8, that with the malt amylase was carried out at a pH of 5.5. Results are shown in Table I.

An evaluation of the experiments results in the following interesting observations:

It is evident that the use of a greater excess of enzyme will not, by itself, completely convert the precipitated starch. Also, the lower the temperature, the greater is the residue. It can be seen that, for all the enzymes, there is a greater increase in the amount of residue between 40 and 30°C than there is between 50 and 40°C. The results of the earlier experiment using starch solutions, which indicated that it was not advisable to allow the desizing temperature to drop below 40°C, were completely confirmed by the conclusions drawn from the new experiments made with swollen starch. This also explains why, with the addition of the usual quantities of enzyme and with the normal starch-sized cloths, an iodine test gave violet or red-violet coloration before washing rather than the hoped-for yellow. On the other hand, it also shows that there is no important difference between the individual enzymes at 40 and 50°C provided they are added in sufficient quantities and the reaction allowed to proceed to the end point of the conversion. This may vary from 6 to 18 hours. This is more clearly apparent if the enzymatic conversion is carried out on a starch film rather than on precipitated, pulverized starch. The starch film is allowed to stand quietly for a few hours at a given temperature in a desizing solution. Under these conditions the film maintains its shape. If it is but slightly stirred with a glass rod it disintegrates at once. Not only does the enzymatic desizing effect the conversion of the greater portion of the starch into water-soluble products, but it also causes a corresponding decrease in the solidity of the insoluble portions. It is therefore evident that it is not necessary for the enzymatic conversion to proceed until complete solubility is reached, but only so far as is necessary to weaken the solidity of the starch film so that it has no great resistance to mechanical washing. The washing of the enzymatically desized fabric depends not only upon soaking in cold or, better yet, warm water, but just as much on the mechanical action of the rope washer. This treatment creases the fabric. If this is undesirable, the washing is done on an open-width washing machine, and a heavy stream of hot or cold water is sprayed over it.

Compared to the pancreatic amylase the malt amylase exhibits a definitely slower action even with the addition of considerably more enzyme. The conversion with 0.2 g of malt amylase containing 0.21 AU at 40°C is appreciably less than with 0.1 g of pancreatic amylase containing 0.18 AU or 0.1 g bacterial amylase containing 0.04 AU. With the malt amylase there remained a residue of 33% after two hours whereas the other two enzymes yielded a residue of only 17.5-19.0%. Only after a very long reaction period did this difference even out to some degree. These characteristics of the malt enzymes become still clearer if one observes their behavior at 30°C. At this point it is clearly recognizable that the malt enzymes are more strongly dependent upon temperature than are the other amylases. This peculiar behavior of the malts induced us to make a further study of this question in order to find an explanation for it.

TABLE I

Amount of enzyme	Temp (°C)	Amylase — Bacterial	Amylase — Pancreatic (% residue)	Amylase — Malt
CONVERSION TIME: 2 HOURS				
0.1 g	50	10.9	13.8	19.0
	40	19.0	19.9	37.7
	30	29.2	30.3	55.0
0.2 g	50	10.9	12.0	19.7
	40	19.1	17.5	33.1
	30	27.5	24.0	46.0
SAME EXPERIMENTS HELD OVER NIGHT				
0.1 g	50	8.5	10.8	12.5
	40	15.4	16.0	22.2
	30	24.4	25.1	39.0
0.2 g	50	8.8	10.3	11.9
	40	14.2	14.4	18.0
	30	25.2	25.2	32.3
0.3 g	50	9.2	9.1	11.0
	40	13.7	13.8	17.6
	30	22.2	22.0	29.2

The malt enzyme occupies a special place among the enzymes used in desizing. Whereas the bacterial and pancreatic amylases consist of a single amylase insofar as we know today, the malt enzyme consists of two different enzymes that react differently, ie, an alpha and a beta amylase. From a determination of their Willstaetter Values they are found to be present in malt in the ratio of 1.5 to 1.6; ie, in a commercial malt containing 1.04 AU/g about 0.17 to 0.21 AU is alpha amylase and 0.87 to 0.83 AU is beta amylase. It seemed logical to assume that the basic reason for the peculiar behavior of the malt could be sought in this characteristic, which made it different from the other enzymes.

We investigated this question very thoroughly by testing alpha and beta amylases individually and together on precipitated starch at temperatures of 50 and 30°C. For this purpose we prepared beta amylase containing 7.85 AU/g from malt by treating it with acid, and from the same malt we obtained alpha amylase by treating it with heat. The strength was 1.6 AU/g.[a]

In this way we recovered 0.031 g beta amylase corresponding to 0.243 AU and 0.025 g of alpha amylase corresponding to 0.04 AU.

Table II shows clearly that the conversion effected by the beta amylase lags considerably behind that of the alpha amylase, particularly in those tests run at the lower temperature. Even at 50°C the rate of conversion of the alpha amylase is a multiple of that of the beta amylase.

[a] Investigations which have been confirmed by others have, meanwhile, shown that beta amylases purified in this manner are not completely pure but still retain in very small amounts enzymes which are able to split branches of the starch molecule. The effect of these enzymes is only noticeable after a long period of time. Therefore they are not so important to the results obtained in the two-hour period.

TABLE II

Reaction time (hrs)	Temp (°C)	Amylase		
		Alpha	Beta (% residue)	Alpha + Beta
2	30	41	95	46
18	30	24	84	22
2	50	15	68	11
18	50	11	24	10

Therefore it is clear that the dependency of the malt amylase upon temperature is not, as was originally assumed, due to the beta amylase but can more rightly be traced back to the alpha amylase. This is not surprising since the pancreatic and bacterial amylases show certain differences in the effect of temperature, which are shown in the figures given earlier.

As shown above, the higher the temperature the more complete is the conversion of the starch. It is feasible to assume that the reason for this is to be found in the swelling of the starch, which is certainly better at 50°C than at 30°C. To test this assumption we tried:

A) 3.2 g of precipitated starch with 120 cc of enzyme solution (pH 6.8) containing 0.1 g of bacterial amylase of 0.4 AU/g strength at 30°C.

B) The same experiment at 50°C.

C) Finally, we heated the starch 15 minutes in 100 cc of water at 50°C, then cooled it to 30° and then added 0.1 g of bacterial amylase (0.4 AU/g) and 20 cc of buffer solution.

All the mixtures were held at the reaction temperature of 30 or 50°C for 16 hours and then centrifuged. The residues were washed as usual, centrifuged and dried. In an additional experiment starch was treated the same as above except that no enzyme was added. The percentage of water taken up by the starch was calculated on the dry starch. The following results were obtained:

	A	B	C
Water absorbed (%)	295	403	390
Insoluble residue (%)	31.6	10.9	22

(Percentages based on the dry starch used.)

From the above figures it is apparent that the degree of water absorption is the same in experiments B and C and that, therefore, the enzymatic action takes place under the same conditions in this respect. Nevertheless, the conversion at 30°C of the swollen starch in experiment C does not proceed as far as that in experiment B carried out entirely at 50°C. This shows that it is not the degree of swelling alone that controls the degree of conversion. There must be other contributing factors. It is possible that large molecular groups in the precipitated starch, which were formed by agglomeration of individual molecules, are, in the presence of water, more apt to break down again into individual molecules at 50°C than at 30°C. These individual molecules are more easily attacked by the enzymes than are the large molecular groups. This is why the action of the enzymes is more energetic at 50°C than at 30°C. It follows, therefore, that in desizing it is desirable to keep the temperature as high as possible. If the specific type of enzyme used does not permit this, the starch should be preswelled to as great an extent as possible by soaking in hot water. This process has been proven the best in practice.

The experiments which have been described so far have been based upon the assumption that the entire quantity of enzyme solution absorbed by the cloth is available for the conversion, and also that the partial conversion products are evenly distributed in the enzyme solution. This condition is doubtless the case if the desizing is carried out in a vessel where care is taken to provide adequate circulation for the addition of the enzyme and removal of the conversion products. In desizing on a jig, and especially in the layover, this relationship is much different and there is some question as to whether the experimental procedure selected does present a true picture. The starch to be converted is not evenly distributed throughout the fabric but is found only in the warp threads. Therefore the question arises as to whether only the enzyme solution absorbed by the warp takes part in the desizing or whether that in the filling is available also. Owing to its greater absorptive capacity, the filling holds more enzyme solution than the warp. The ratio between the two is a function of the type of fabric. For our purposes, we assume that for every 100 parts of warp fabric there were 6 parts of starch and that the fabric absorbed 100 parts of liquid containing 0.1 to 0.2 parts enzyme. This ratio did not seem in complete agreement with the conditions in common practice. Therefore we tried to find out how the conversion would progress using less enzyme solution.

In order to clarify this relationship, we used the same amounts of enzymes in some of the tests that we had used in the earlier experiments, and in others we used half the quantity of enzyme. Naturally the first series of experiments had a higher concentration of enzyme solution which approximated the concentration used on a jig, but was not like that used on a layover. In the latter case, there would be a still further decrease in the enzyme concentration equalling about 1 to 2 g/l of the commercial enzyme.

In our tests, we dissolved the enzyme in 20 cc of water and added this solution to a slurry of starch in water or buffer solution. The additional quantity of water varied between 0 and 100 cc when 3.2 g of precipitated starch was used. Our object in the first tests was to determine the effect of decreasing the amount of liquid.

To 3.2 g of starch, we added 0.1 g of bacterial amylase dissolved in 20 cc of water. The pH was 6.8 and the times of reaction were 2 and 18 hours at 50°C.

Water (cc)	% Residue	
	Reaction time—2 hrs	Reaction time—18 hrs
100	13	9
50	11	8.5
20	16	11.5
0	23	14

Other amylases which we tested in the same way gave similar results. All of them showed that, at a constant ratio of starch-to-enzyme and with a decreasing liquid ratio, the conversion is first accelerated and increased and the optimum ratio is approximately one part of starch to 70 parts solution. If the amount of liquid is decreased any further, there is a definite retardation of the enzymatic action both with respect to the degree and rate of conversion. This retardation of the enzymatic action might be caused by the conversion products. In a ratio of 1:15 to 1:7 it is especially marked. Therefore we investigated this range more critically and also varied the amount of enzyme. We used the same enzymes which had been used in the earlier experiments.

The quantities used were as follows:

A) 0.1 g of enzyme with 3.2 g of starch in 45 cc of buffer solution.

B) 0.05 g of enzyme with 3.2 g of starch in 45 cc of buffer solution.

C) 0.1 g of enzyme with 3.2 g of starch in 20 cc of buffer solution.

D) 0.05 g of enzyme with 3.2 g of starch in 20 cc of buffer solution.

The usual phosphate buffer was used. The buffer was adjusted to pH 6.8 for the bacterial and pancreatic amylases and pH 5.5 for the malt amylase. The reaction time was 2 hours and the temperature 50°C.

Amylase	% Residue			
	A	B	C	D
Bacterial	18	19	21	23
Pancreatic	17	17	19	18
Malt	24	23	30	34

An overnight test gave the following results:

Amylase	% Residue			
	A	B	C	D
Bacterial	14	16	18	19
Pancreatic	14	18	18	19
Malt	14	19	17	21

The conversion was tried at 30°C. Since the temperature was so low, it was run for an 18-hour period only. At that temperature, a 2-hour layover would be useless.

We ran two sets of experiments, A and

B. In A we used 0.1 g of bacterial, pancreatic and malt amylase with 3.2 g of starch and 45 cc of water, and in B we used the same amounts of enzymes in 20 cc of water.

Amylase	% Residue A	% Residue B
Bacterial	31	32
Pancreatic	30	33
Malt	35	36

These experiments showed us that using smaller amounts of liquid definitely caused a decrease in the activity, especially if, as in these experiments, high concentrations of enzymes were used. These differences were partly compensated for if the reaction time was long enough. This retardation is especially high with the malt amylases and still very marked at 50°C. It is clearly shown, and practice confirms it, that these enzymes are less suitable for rapid desizing but are suitable for overnight layover. To be sure, they did not proceed any further here than the other enzymes even though optimum conditions were maintained in our experiments. This is also in agreement with the technical processes.

It was shown that the malt amylases, when added in the same quantities as the other enzymes, do not produce any greater degree of conversion. If, in a treatment of several days, the malt amylases show a greater degree of conversion, it is our opinion that it is due primarily to the extensive growth of bacteria or mold. In the latter case, the dreaded spotting of the goods may occur. Because the layover bin is contaminated with acid-forming organisms, considerable amounts of lactic acid are formed very rapidly as well as glucosidases, which also convert the residual dextrine that has not been converted entirely by the amylases.

A question which is of considerable importance in practice is that of rapidity of conversion. We investigated this with tests on both precipitated starch and a starch film. The results obtained were rather surprising. As in the previous experiments, we used 3.2 g of starch, 120 cc of water and 0.1 g of bacterial amylase at 50°C. In order to get comparable results, we sifted out the smallest size particles (0.1 mm) and the largest size particles (0.3 mm). The enzymatic action was stopped at definite intervals and the undissolved portion of the precipitated starch was determined.

Time (mins)	Residue (%)
10	13.0*
20	13.6*
30	14.7
60	14.3
90	13.5
120	13.1
180	12.8
300	12.3

* The somewhat lower residue found in this experiment after 10 and 20 minutes consistently occurred and was also found when other enzymes were used. The cause of this peculiar phenomenon is not yet clear, but it is assumed that the values at 10 and 20 min are too low. (Compare with *(2)*).

A residue of 91.2% was obtained from a blank run for 30 minutes using no enzyme. As a control, we used a mixture containing a very finely divided starch film. The time intervals selected were somewhat different.

Time (min)	Residue (%)
10	58
30	39
120	10

In this instance, there were definitely observable differences between the precipitated starch and the starch film. Whereas the conversion with the precipitated starch went surprisingly quick and the end point was very nearly reached after a few minutes (differences in the results were traced back, in part to experimental error), the conversion of the starch film, run under identical conditions, took much longer to reach the same end point. This is very important in evaluating the tests. The conversion experiments were carried out on starch films, using 0.1 g of enzyme and 3.2 g of starch film. (See Table III.)

In the face of these relationships, it is naturally difficult to say anything concerning the speed of conversion on fabric. Apparently there are two limitations with the powder and film used here. On the one hand, it is not to be assumed that the film in the fabric has as large a surface as the precipitated starch. On the other hand, it has been proven here that, with the comparatively thick films, the ratio of surface-to-weight is apparently less advantageous than in the sized fabric. But even under these unfavorable conditions, it was established that the conversion proceeded to the possible limit after about 2 hours at 50°C. Therefore, it may be said that, in all probability, the limit is reached after 2 hours on the fabric also. To be sure, this conclusion is valid only if there is a sufficient amount of liquor to dissolve away the conversion products. As stated above, these conditions exist only in tub desizing. Therefore, we considered it only right to investigate the behavior of starch films with enzyme solutions using smaller amounts of water.

The conditions selected for the experiments were the same as before. To 3.2 g of starch film with a water content of 10% was added 0.1 or 0.05 g of bacterial, pancreatic or malt amylase in 45 and 20 cc of buffer solution. Table IV shows the residues remaining after a reaction period of 2 hours at 50°C or 18 hours at 30°C.

If the results obtained from the conversion of the starch film using smaller amounts of enzyme are compared with those obtained under similar conditions with precipitated starch, they are seen to lie very close together. They show that, with decreased amounts of liquor and enzyme, the conversion goes tolerably far and, indeed, the higher the temperature, the further it proceeds; but in no case does it lead to complete solubility of the starch. In practical work, an aftertreatment is required to remove the residue. This can be carried out in various ways by washing with water or a soap solution, as has been discussed above. Kier boiling with alkali acts in the same way. This aftertreatment is effective only if the starch has been sufficiently acted upon by the enzymes, since the solubilizing process quickly ceases in the case of unconverted starch due to the great increase in the volume of the starch.

Although the above experiments were carried out on sample materials and were, therefore, subject to certain variable factors, we believe that they will nevertheless be comparable to what is found in practice.

SUMMARY——The following conclusions may be drawn from our experiments:

TABLE III

Time (hrs)	Temp (°C.)	Amylase: Bacterial	Amylase: Pancreatic (% residue)	Amylase: Malt
2	30	58	61	71
2	50	10.5	13	14
18	30	27	29	34

TABLE IV

Amount of enzyme (g)	Amount of buffer solution (g)	Amylase: Bacterial	Amylase: Pancreatic (% residue)	Amylase: Malt
	2 HOURS AT 50°C			
0.1	45	16	14	18
0.1	20	16	16	18
0.05	45	23	33	37
0.05	20	23	29	31
	18 HOURS AT 30°C			
0.1	45	32	33	37
0.1	20	31	34	35

In the enzymatic conversion of undissolved starch as found in sized fabrics, complete solution of the starch is not accomplished by addition of larger quantities of enzyme. The amount of undissolved starch depends more upon the desizing temperature than upon the quantity of enzyme. Temperatures below 40°C should be avoided if possible. Adequate swelling of the starch is a prerequisite to good desizing. Under conditions such as are met with in desizing on a jig, the desizing is completed in about 2 hours. In the layover method, desizing takes a longer time because of the retardation which takes place.

NEW TYPES OF AMYLASES

Generally speaking, before World War II only those amylases which consisted of mixtures of enzyme concentrates with rock salt and Glauber's salt and perhaps a small amount of added stabilizer were known. In the years following, an attempt was made to improve the desizing agents by putting in additives of various types. In the main, these attempts fell into one of two categories. On the one hand, investigations were undertaken with a view to increasing their stability in storage and, at the same time, to increase their stability to heat. Secondly, work was done on setting the optimum pH to improve the activity of the enzymes.

One way to increase their resistance to higher temperatures and, at the same time, increase their stability in storage in a humid atmosphere is set forth in a publication of the Schweizerischen Ferment A G, Basel *(3)*. According to this publication, desizing agents are classified by their content of amylase, rock salt and calcium sulfate. The latter may be in the form of gypsum. The calcium sulfate is supposed to increase the resistance of the amylase solution to heat as well as to increase the stability of the dry preparation to damp air. As far as is known today (whether this can be patented is still contested), the solutions of amylases containing gypsum show no greater resistance to heat than solutions of other calcium salts of the same molar concentrations. Calcium formate had already been used earlier for this purpose. This is really not surprising since the action of the calcium salts depends primarily upon their ability to precipitate the destabilizing components. This is accomplished only by the calcium ion and not by the anion to which the calcium is joined. Even so, it is not entirely clear why these products should exhibit a greater stability in storage in the presence of dampness than those amylase preparations which, up to now, had contained considerable amounts of anhydrous sodium sulfate, which dehumidified the air.

A much more original method is described in the same publication *(4)*. In addition to the methods mentioned previously, the ferment mixtures should contain vegetable protein in the form of lupine, bean, soya bean or vetch meal. Specifically mentioned are combinations of pancreas extract with these meals, which are supposed to exhibit a great stability in storage. A disadvantage of the described process is that these stabilizers are insoluble.

Another publication *(5)* also is concerned with the increase in stability at higher temperatures, especially in distilled water. In this case, also, calcium salts were used to make the amylases resistant to heat. It is not difficult to stabilize solutions of enzymes containing no sulfate against high temperatures if considerable quantities of soluble calcium salts are added. In practice, however, there are difficulties since in all dry amylase preparations there are considerable amounts of anhydrous Glauber's salt present to stabilize them in storage in a humid atmosphere. When these preparations are dissolved in water, the calcium salts are immediately converted into calcium sulfate. Therefore, there is only enough soluble calcium salt put into these amylases to form the amount of calcium sulfate which can be dissolved. It follows, therefore, that the calcium concentration necessary for optimum stability is never attained.

In this publication *(5)* it is proposed that a small amount of a soluble silicate in addition to the calcium salts be added to the amylases containing sulfate. The effect obtained in this way is most clearly evident with a bacterial amylase. If 65 mg of calcium formate and 60 mg of sodium metasilicate are added to 2 g of a commercial bacterial amylase of a strength of 0.4 AU/g dissolved in distilled water, the same temperature stability will result as would be attained by the addition of 3 g of calcium formate alone. This is easily demonstrated by measuring the decrease in AU when the solution is heated. In a desizing experiment the action of the silicate is somewhat less since the starch present in the fabric has a certain stabilizing effect.

Some work has been done also in the United States on increasing the stability in storage. There is greater emphasis on this in the United States than in Europe since dry amylases are used very little. For the most part aqueous solutions are used, which are rather more susceptible to spoilage than are the dry commercial products of Europe. It has been found that the storage stability of some types of solutions can be increased if thioformamides of various types are added to them *(6)*.

In addition, it must be mentioned that experiments have also been made on varying the pH of the amylase solution in order to increase its activity. It is known that every amylase has an optimum activity at some given pH. Up to now, the correct pH has had to be adjusted, eg, in the malt amylase, by adding acetic acid, which is usually considered a nuisance. Recently, bacterial amylases have been put on the market, which contain monosodium phosphate in addition to the neutral salts. When they are dissolved in water in the usual concentration, the resulting solution has a pH very near that necessary for optimum activity. In the case of the bacterial amylases, this would be pH 6.5.

Before the currency reform, mold amylases were also available in the German market. At that time, they possessed a certain importance owing to the scarcity of other amylases. Because of the appearance of abundant quantities of the pancreatic and bacterial preparations, the mold amylases soon disappeared from the market, but they are again assuming importance in a new and improved form. For a mold amylase, they exhibited considerable resistance to heat, but they were not more stable than the bacterial amylases. Regarding the preparation of the related mold as well as the other conditions of manufacture, there is not much known. The future must show whether they will be able to compete with or replace the bacterial amylases.

NEW DESIZING PROCESSES

The further development of desizing processes concerns open-width and continuous desizing. The object is to desize fabrics as rapidly and as completely as possible, and in this way, to avoid creasing of the fabric. Creasing is unpleasantly noticeable after a fabric is dyed in light shades.

It has been shown that the conversion proceeds relatively quickly on the small particles, which are easily accessible from all sides, and that the solubilization of starch films does not require too long a time, especially when the fabrics to be desized are tightly woven. Therefore, it is clear that enzyme solutions alone are not able to sufficiently solubilize the starch in a few minutes to the point where it can be leached out by a washing or boiling treatment alone. All processes for rapid desizing on the open-width washer depend, therefore, upon the action of an enzyme plus supplementary treatment to complete them.

One of the oldest processes for this purpose has attained a certain amount of importance. It consists of passing the material to be desized through hot water, which should contain a wetting agent to improve the wetting action. This causes the starch to swell considerably, which facilitates the action of the enzyme. After the fabric is squeezed out as much as

possible, it is led through a bath containing about 2 to 5 g of a commercial bacterial amylase (0.4 AU/g) at a temperature of 65 to 70°C. Because of the great amount of swelling of the starch, it is not transformed into water-soluble condition within the few minutes allotted, but it is converted to the extent that it is easily soluble in a warm, dilute lye solution. Untreated starch is hard to dissolve in a warm, dilute lye solution. The bath with the amylase solution is followed by a bath containing dilute waste lye, a hot water bath and a bleaching bath. This process is important only in relatively slow-running machines.

Another desizing process has found considerable favor in the United States. The basic thought behind this process is that, with the J box, the period of activity of the enzyme can be considerably lengthened without the equipment becoming too big to handle. The fabric is impregnated in the open width with an enzyme solution of the same concentration as above. It is squeezed out and led into a J box. Before the fabric is impregnated with the amylase solution, the starch may also be swollen by treatment with boiling water. If this is done, the concentration of the enzyme solution must be kept somewhat higher than if the starch were not preswollen. The subsequent treatment in the J box can be accomplished in several ways: either steam is blown into it from the bottom or it is heated from the outside. In the first case, it is easier to attain a higher temperature, but there is also high moisture content in the fabric, which is not always desirable. In the second case, there is danger of a crust forming on the sides of the J box, and eventually there may be damage due to formation of dried-out spots. It is better to insulate the J box. There is no advantage in letting the hot enzyme solution trickle over the fabric. Since the time in the J box is about 20 minutes, a very thorough desizing takes place, provided an enzyme solution is used that is not too dilute. By subsequent washing in very hot water, followed by a bleach, complete desizing can be obtained. This process gives good results. A disadvantage is that, in the case of extremely delicate fabrics, such as certain rayon specialties, there is danger of cracking during treatment in the J box. This is more noticeable in light dyeings. Even so, this type of treatment also has found a certain degree of favor in Germany.

The theory behind a third process *(7)*, which has been little tested, is that, after its saturation with a diastatic-acting enzyme solution, the textile to be desized is subjected to a sudden local rise in temperature in a heating chamber, on hot cylinders or in some other suitable manner. With this method, there is a noticeable conversion of the starch within a few minutes, which under the usual conditions could be attained only after a much longer period of time. One requirement for the success of this process is that fairly definite narrow limits must be maintained. First it requires a fairly high enzyme concentration [about 7-12 g of a normal bacterial amylase (0.4 AU/g) per liter]; secondly, the fabric must be heated to 90-95°C, and be kept very moist. Higher temperatures are harmful but, on the other hand, lower temperatures do not permit a fast desizing. The higher enzyme concentration is necessary primarily to counteract the retardation caused by the conversion products, which slows up the desizing, as explained in the theoretical part of this article. For the same reason, it is necessary to keep the fabric moist during the desizing, for if the fabric dries out too much, the concentration of the conversion products rises and the retardation increases; secondly, at high desizing temperatures, the amylases are quickly destroyed and a considerable excess is required to maintain a satisfactory concentration.

It may seem somewhat surprising to those conversant with enzymatic desizing processes that desizing temperatures of about 90 to 95°C are used, all the more so since manufacturers of bacterial amylases warn against heating the enzyme solutions to temperatures in excess of 70°C. In spite of this, there is no contradiction since the enzymes are, for the most part, not in free solution, but are loosely bound to the starch present in the fabric; in this way they are stabilized. There is no point, therefore, to working with large amounts of liquor at these high temperatures since the amylases in the solution are not stabilized and would be destroyed. Anything other than the enzyme solution with which the fabric is impregnated is superflous. A preswelling with boiling water is pointless since this would reduce the high concentration of the enzyme in the fabric so necessary for good desizing by the steam process. In practice, the fabric is led through a mangle, the trough of which contains a solution of 7 to 12 g/l of a commercial amylase at 60 to 70°C. The pH of this solution is adjusted to 6.3 to 6.5. If it is necessary to lower the acidity, lye or aqua ammonia is added in small amounts. For a neutral pH in the amylase solution, acetic acid is added. The trough of the padder should be as small as possible (100 to 150 liter capacity) in order to keep the consumption of amylase as low as possible due to the necessity for a higher concentration of the amylase solution. If these conditions are maintained, then the use of amylase is no greater than in desizing processes in use up to now. The fabric passes through the solution at the rate of about 55 ypm, is squeezed out after sufficient impregnation at the ratio of about 1:1, and is then led through a steamer, with the temperature kept between 90 and 95°C. The steam should pass through a water bath to keep it very wet so that the fabric can leave the steamer with the same moisture content it had when it entered. The steaming time is about 3 to 4 minutes. At the conclusion of the steaming, the fabric is washed at the boil in the usual way and, if necessary, it is bleached. At this point, it is virtually starch free.

CONCLUSION

This concludes the survey of the development of desizing in the period after the war. It is abundantly clear that, in the last few years, considerable progress has been made in every direction.

REFERENCES

(1) Willstaetter, Waldschmidt, Leitz and Hesse, *Z physiol Chemie*, 143 ff (1923).

(2) Lulla, B S, *Research* 3, 290-1 (1950).

(3) Publication of the Schweizerischen Ferment A G (Basel), p3266 B 8k, 1/04 (June 18, 1949).

(4) *Ibid*, p3267 B 8k 1/04.

(5) Publication of Kalle & Co (Germany), K 13,314 IVa/6a, 22/04.

(6) U S Pat 2,567,747, Wallerstein Co, Inc, New York, N Y.

(7) German Pat 448,494, Toman and Jenny.

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ABSTRACT

The Rotproofing of Viscose Rayon: I. Treatment with Formaldehyde and Formaldehyde-containing Resins

Bell, J W, Ramsey, M M and Whewell, C S, *J Soc Dyers Colourists* 71, 660-7, November, 1955.

Cellulosic fibers are widely used in the manufacture of fabrics which are destined to be employed under conditions entailing exposure to attack by microorganisms. Wastage due to rotting reaches particularly serious proportions in tropical climates, and much research has been conducted on methods of rotproofing cotton fabrics. Little attention, however, has been given to rayon.

The authors have investigated the effect of crease-resist processes in increasing the resistance of viscose rayon to microorganisms. Following is a summary of their results:

Viscose rayon yarn was treated with formaldehyde and a number of formaldehyde-containing resins, and exposed to cultures of certain destructive microorganisms in a laboratory incubator, in an attempt to obtain a rotproof finish. The most outstanding result that emerges from the experiments is that halogenated phenoplasts are more efficient than either urea-formaldehyde or phenol-formaldehyde, and that a resin prepared from bromophenol and formaldehyde is exceedingly effective, a deposit of only 5% on the yarn being resistant to microorganisms under the most severe and prolonged test conditions. It also appears possible to improve the efficiency of urea-formaldehyde resin by incorporating a small proportion of halogenated resin.

Urea-formaldehyde resin by itself is effective only if present in prohibitively high concentrations; below 15-20% the proof breaks down on prolonged testing. Formaldehyde alone is moderately effective, and appears to have little effect on the wet tensile strength of the viscose rayon; it may be of value where conditions highly favorable to the growth of microorganisms are not likely to be encountered.

The experiments have shown that laboratory assessment of rotproofing should be carried out by more than one method; a treatment that confers a measure of resistance to microorganisms under one set of test conditions may be much less effective when tested by a different procedure. This confirms the findings of many other workers.

Fourteen references to the literature are cited.—WHC

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Philadelphia, Mid-West and Niagara Frontier Sections——

SEQUESTERING AGENTS IN WOOL AND COTTON DYEING*

HENRY E MILLSON
American Cyanamid Co
Organic Chemicals Division
Bound Brook, N J

INTRODUCTION

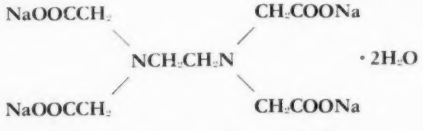
THERE is considerable interest at present in the use of sequestering agents as aids in the production of brighter and true-to-tone shades on wool and cotton. In the dyebath, the presence of traces of metal ions, such as aluminum, copper, iron and manganese, can cause the shade of many dyes to appear dull and off-tone. Chromable dyes usually react with such metal ions to form dye-metal complexes having shades and fastness properties different from those of the dye-chromium complex. Sequestering agents are used to prevent the formation of such undesirable dye-metal complexes, making it possible to obtain brighter shades with unimpaired fastness properties. Dyes also react with these metal ions to form insoluble dye salts called *lakes*. These resulting precipitates are often adsorbed on the fibers and cause excessive crocking. Sequestering agents can prevent or reduce this danger.

Certain precautions must be taken in the use of sequestering agents, particularly when using chrome or metalized dyes. Sequestering agents can produce undesired effects by preventing the desired metalization or cause demetalization of dyes which contain metal as a component part of the molecule. When this occurs, it is generally accompanied by a change in shade and a decrease in fastness properties.

DISCUSSION

CHARACTERISTICS OF SEQUESTERING AGENTS———Sequestering agents are chelating compounds, which react with metal ions to form stable water-soluble metal complexes that do not react with dyes. Metalizable dyes themselves are efficient chelating compounds and are often quite resistant to subsequent demetalization. Textile fibers, especially wool, have considerable affinity for metal ions, removing small amounts rapidly and completely from the dyebath and holding them tenaciously. There are two possible ways in which metal ions can react with dyes: 1) by forming a chelate or dye-metal complex similar to the complexes which are formed when chromable dyes are chromed, and 2) by replacing hydrogen in the sulfonic acid group on the dye molecule. The first reaction occurs only with dyes which have a specific type of structure. When reacting with metal ions, sequestering agents cause these ions to combine in such a manner that they can no longer react with the dyes to form either complexes or salts.

There are several classes of compounds which will act as sequestrants of metal ions *(2)*. Among the better known types are citrates, oxalates, tartrates, polyphosphates, hexametaphosphates and the sodium salts of ethylenediaminetetra acetic acid. These tetra acetic acid compounds are sold as Trilon B, Kalex, and as the Sequestrenes and Versenes. The structural formula of the tetra sodium salt of ethylene diamine tetra acetic acid is generally given as follows *(1)*:



Oxalic, tartaric or citric acids may form more stable complexes with the metal ions than do the dyes, and it is this stability which makes these compounds difficult to use in certain dyebaths. In some cases, these acids demetalize desirable metal-dye complexes, such as the metalized wool and copper-containing direct dyes, thereby changing their shade and fastness properties. The sequestering of undesirable metal ions during the application of chromable dyes without interfering with the subsequent desired metalization of the dye requires care in the selection and use of the chelating compound.

SOURCES OF METAL CONTAMINATION———As has been reported previously *(3, 4, 6, 7, 8, 9)*, interfering metals can be introduced into the dyebath in many ways. Dyehouse waters may become contaminated in nature by contact with rocks, minerals, soils, vegetation and bacteria, and in the mill by pipes, machines, dyes and chemicals.

1) *Contamination by Natural Means.* As underground waters travel, they dissolve small amounts of mineral matter from the soils and rocks with which they come in contact. Their dissolving capacity may become considerably increased by the presence of dissolved gases, such as carbon dioxide or other gases from decaying vegetation, particularly when these are acidic in nature. Percolating rain waters containing gases dissolved from the air and soil also serve as contributors to the contamination of ground waters The underlying minerals in many areas of our continent where textile mills are located are limestone ($CaCO_3$) and dolomitic limestone ($CaMg(CO_3)_2$). These minerals are generally responsible for the well-known calcium and magnesium hardness in ground and well waters. However, in addition to their calcium and magnesium content, these limestones may have an iron and manganese content which, expressed as oxides, ranges from 0.7% to 2.60% for iron and from 0.5% to 1.0% for the manganese, depending upon the locality. Clays generally contain considerable iron and some aluminum, which are derived from the weathering and disintegration of the parent rocks. Ground waters gradually solubilize and extract the metallic-ion content from such soils. Chemical analyses have shown that the mineral or metal impurity content of water will vary widely, depending upon the locality and composition of the minerals in the area, the method of purification, and the conditions of transportation.

Minerals and soils are, therefore, potential sources of metal-ion contaminants which, if not removed prior to use or sequestered in the dyebath, may cause

* Presented before the Philadelphia Section on October 28, 1950; the Mid-West Section on April 10, 1954; and the Niagara Frontier Section on October 8, 1954.

NOTE: The following are trade-marks of the American Cyanamid Co: Calcochrome, Calcocid, Calcofast, Calcomine, and Calcosyn. Decerosol is a registered trade-mark.

precipitation of the dye, dulling, or other undesirable shade and fastness changes.

The so-called iron bacteria found in natural ground and surface waters are bacteria *(10)* have the ability to remove minute quantities of iron from the waters in which they grow and convert it to iron hydroxide. This is done as a phase of their life process, during which time they deposit the insoluble iron hydroxide on their outer surface. These bacteria form colonies, which cling to the inside surfaces of pipes, wells and tanks, often clogging the pipe lines. These accumulations are often removed by the force of the flowing water and are carried into the dyeing or rinsing baths. When such deposits enter dyebaths having a low pH, as in wool dyeing, the iron hydroxide is dissolved to form iron ions, which can react with dyes, causing dullness of shade and inferior fastness properties. These organisms also are capable of using manganous salts in a manner similar to that of iron *(16)*. Both iron and manganese are undesirable trace metals and should be removed from the water or inactivated in the dyebath.

2) *Contamination in the Mill.* In addition to the mineral salts which may have been acquired naturally by the water, trace amounts of metals may also be introduced during processing. For example, aluminum or iron salts are often added during water purification processes to form metallic hydroxide gels, which remove organic material from the water, and traces of these gels may remain after the purification process is completed. Iron may also be present from the corrosion of the water pipes or steam lines.

Older dyeing machines still in use have been constructed from one or more metals, such as iron, copper, aluminum, brass and bronze. Traces of these metals dissolve and can cause trouble. Dye and acid pails, dippers, brass spigots and iron drums in which dyes are often dissolved also are potential sources of undesirable metal ions. Complete freedom from contaminating metal ions in processing equipment will not be achieved so long as steam and water pipes are made of iron and dyeing machines are fabricated from aluminum or from alloys containing iron and nickel.

Frequently the technical grades of Glauber's salt that the dyer uses are contaminated with iron, thereby becoming a potential source of dyeing faults. Even the dyestuffs that the dyer uses may contain traces of metal impurities, despite the rigid controls set up by the dye manufacturers for the purification of intermediates and the careful selection of construction materials.

Wool may contain copper as an impurity since cupric sulfate is an important chemical in sheep dips. Lime-pulled wool often contains a high percentage of calcium salts, which may cause precipitation of dyes by lake formation.

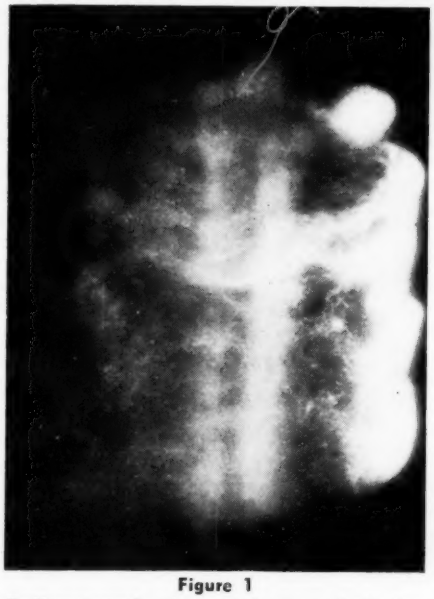


Figure 1
Radioautograph of a staple from Australian fleece in contact with film 2½ hours

Dyeing Method
10% Calcined Glauber's salt
6% ammonium sulfate
2 ppm of radiocobalt isotope[60]-chloride-acetate mixture
2% Eriochrome Verdone A
Boiled one hour
Liquor ratio 60/1

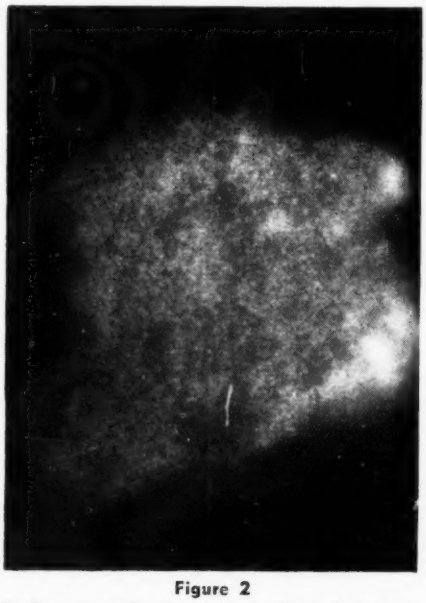


Figure 2
Radioautograph of a staple from Australian fleece in contact with film 48 hours

Dyeing Method
2% Agent #1
10% Calcined Glauber's salt
6% ammonium sulfate
2 ppm radiocobalt isotope[60]-chloride-acetate mixture
2% Eriochrome Verdone A
Boiled one hour
Liquor ratio 60/1

When all such contaminating sources are considered, the wide variations in shade that occur from batch to batch are understandable. Since very small amounts of metal can cause trouble and the concentration of mineral contaminants varies from day to day, there is need for a way to control these impurities in wet-finishing and dyeing processes.

EFFECT OF SEQUESTERING AGENTS ——Modern sequestering compounds are powerful and effective complexing agents which provide a means for control of metal ions. Sequestrants, when used properly, assist the dyer and finisher to obtain the maximum brilliance of shade and effective reproducibility. A large number of organic chelating agents were studied during this investigation and the tetrasodium salt of ethylenediaminetetraacetic acid (34% solution) hereafter called Agent #1, was selected as the standard for this study. Amounts of Agent #1 used during this investigation refer to the 34% commercial strength solution. The percentages expressed are based on the weight of material being dyed. This sequestrant or its other sodium salts will form stable water-soluble complexes with many metal ions, including aluminum, calcium, chromium, copper, iron and manganese. It has been shown previously *(3)* that one part of ionic iron or aluminum in ten million parts of water is sufficient to cause a detectable change in the unmetalized shade of certain metalizable dyes.

The weathered tips of wool fibers usually contain a higher percentage of inorganic matter, especially iron and other metal salts, than the middle and body portions. These metals are concentrated in the tips of the fibers during their growth on the sheep, and thus, when such fibers are dyed, the tips may exhibit the shade of the iron complex of the dye when a metalizable dye such as Calcochrome Alizarine Red SC is applied as an acid color. Previous experiments *(3)* also have shown that traces of metals are removed rapidly from a dyebath, and concentrated preferentially in the damaged tips of wool fibers during the early stages of the dyeing operation. The metal complex of the dye may then be formed in the tips of the fibers and fixed permanently. Although certain cationic and nonionic surface-active leveling agents will prevent the concentration of the metal-dye complexes in the tips, those on the market at present which have been studied do not prevent metalization or the consequent dulling or change of shade. There is, therefore, a need for an effective agent which will sequester undesirable metals,

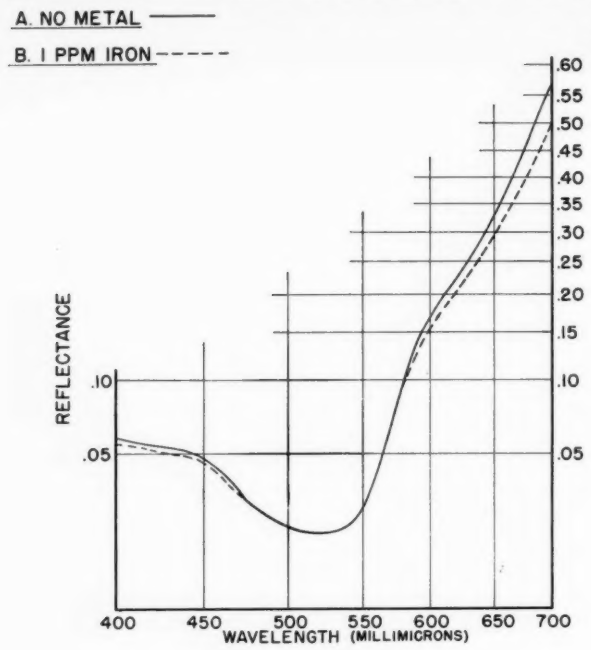


Figure 3
1% Calcochrome Violet B, liquor ratio 10/1

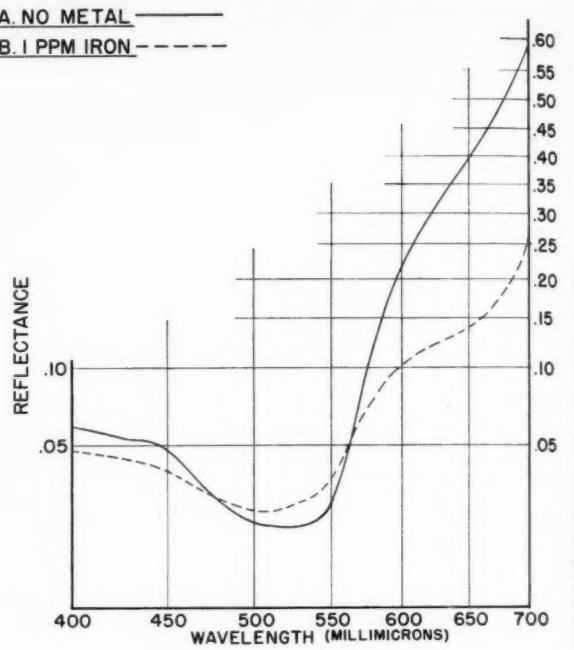


Figure 4
1% Calcochrome Violet B, liquor ratio 100/1

inhibit their absorption by the fiber and prevent reaction with metalizable dyes.

During this investigation, chemical analyses were made on the tips of Australian fleece wool dyed with 2% Calcochrome Violet B (CI 169), with an addition of 3 ppm of iron to the dyebath, with and without 3% of Agent #1. The tips of the fibers dyed without Agent #1 showed the presence of 0.0447% (447 ppm) of iron, while the tips of the fibers to which 3% Agent #1 had been added contained only 0.0098% (98 ppm) of iron. These analyses show that the addition of a sequestering agent effectively prevents the preferential accumulation of iron in the tips of wool fibers.

In another experiment, radiocobalt isotope[60] obtained from the Oak Ridge National Laboratory on allocation from the U S Atomic Energy Commission was employed to determine the efficiency of Agent #1 when used in the application of chrome dyes. Five grams of Australian fleece was dyed in a solution containing 10% Calcined Glauber's salt and 6% ammonium sulfate on weight of material, 2 ppm cobalt, which included 0.1 millicurie of radiocobalt isotope[60], and 2% Eriochrome Verdone A (CI 292). The liquor ratio was 60 to 1 and the constituents were added to the bath in the order mentioned. This dyeing was made in the absence of a sequestering agent. A dyeing similar to the above was made to which 2% of Agent #1 was added first, followed by the other chemicals and dye in the order mentioned above. Both dyeings were raised slowly to the boiling point and allowed to boil for one hour. The wool dyed without the sequestering agent was essentially blue in color (the shade of the cobalt complex) with heavily-dyed blue tips and reddish body. The wool dyed in the bath containing 2% of Agent #1 was reddish brown (the shade of the unmetalized dye), the tips were lightly dyed, while all other areas were heavier and equal in depth of color. There was considerably more radiocobalt in the wool dyed without the sequestering agent. The radioautograph of wool dyed with no sequestrant present (see Figure 1) was exposed for 2½ hours, while the radioautograph of the wool dyed in the presence of 2% Agent #1 (see Figure 2) was exposed 48 hours. It is interesting to note that Figure 1 shows greater development, indicating that the amount of radiocobalt in the wool dyed without the sequestrant is more than 20 times greater than that in the wool dyed with the sequestering agent. Figure 1 also shows more contrast between the tips and body portions of the wool staple.

METHOD OF USE ——— Metalizable dyes form chelate complexes with trace metal ions even at low temperatures. Once the metal complex of a dye has been formed and absorbed by the wool, it may be difficult, if not impossible, to break the chemical-fiber bonding and remove the undesirable metal ions by means of sequestering agents. Therefore, the time to add the sequestrant is prior to the addition of the dye. The material should be run for about 10 minutes with only the sequestering agent present in the bath, then dyeing assistants (Glauber's or common salt, acids, surface-active agents, etc) are added, and finally the dye. This procedure makes it possible for the sequestering agent to inactivate traces of metals by forming stable, water-soluble chelates before they can react with the dye.

INFLUENCE OF LIQUOR RATIO ——— Although the concentration of metal ions present in dyehouse waters is usually expressed as parts per million, this means very little in relation to the effect of these metal ions upon shade, unless the liquor ratio is also stated (3). For example, a dyebath containing 1 ppm of aluminum, copper, or iron at a liquor ratio of 10/1 will contain only one-tenth as many metal ions as a dyebath having a 100/1 liquor ratio. Figures 3 and 4 show the wide difference in shade obtained with 10/1 and 100/1 dyebath ratios on a 1% dyeing of Calcochrome Violet B. Spectrophotometric studies on percent metalization also show that only 4% of the dye molecules are metalized in a liquor ratio of 10/1, while 45% are metalized when a liquor ratio of 100/1 is used. The amount of sequestrant required to prevent undesired shade changes would also vary with the liquor ratio. Figure 5 shows the effect of increasing amounts of Agent #1 on shade and metalization at a liquor ratio of 10/1. Figure 6 shows that these same

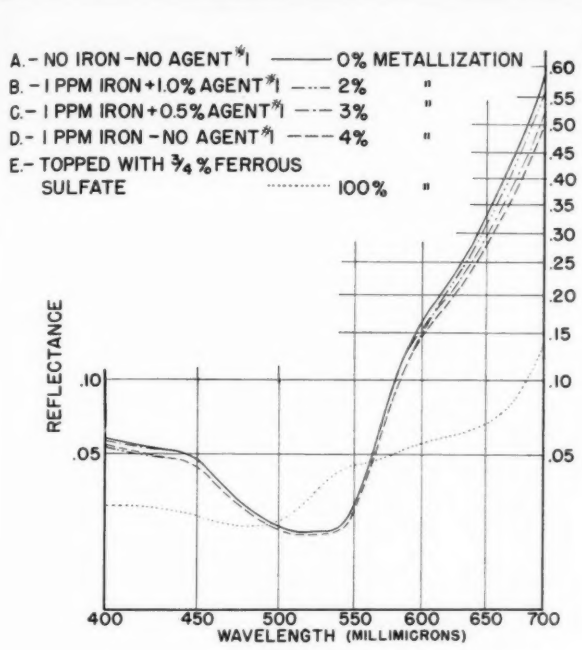


Figure 5
1% Calcochrome Violet B
Percent metalization
Liquor ratio 10/1

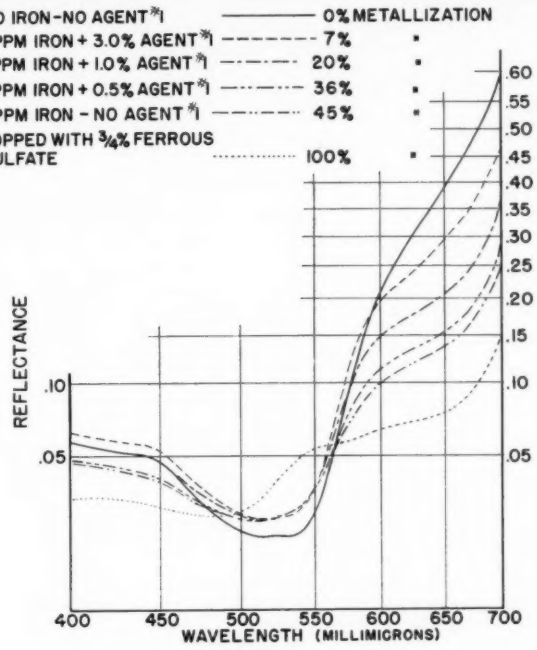


Figure 6
1% Calcochrome Violet B
Percent metalization
Liquor ratio 100/1

amounts are insufficient at a liquor ratio of 100/1 since 3% of Agent #1 is required to reduce the extent of metalization to 7%. Thus, the percent of sequestrant should be increased proportionately with increasing liquor ratio, although the ppm of metal ions remains constant.

These data show that detrimental effects of metallic ions may be minimized by maintaining the lowest dyebath liquor ratio possible.

EFFECT OF METAL IONS AND AGENT #1 ON ACID AND MILLING DYES——Traces of aluminum, copper and iron ions, as a general rule, cause color changes when present in an acid or milling color dyebath. A group of more than eighty dyes, comprising both acid and milling types, was studied to determine the effect of different metals upon their shades. The dyes were applied by methods which produced level, well-penetrated dyeings. (See Appendix in application section listing dyeing methods Nos. 1 to 9). Each color was evaluated by making dyeings with added metal impurities and with and without Agent #1. The metal impurities introduced to the dyebath were aluminum sulfate $Al_2(SO_4)_3.18H_2O$, cupric sulfate $CuSO_4.5H_2O$ or ferrous ammonium sulfate $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ and provided 2 ppm of the respective metal ions. A control dyeing containing no added metal ions was also run.

Only seven dyes were unaffected by any of the three metal ions. The remaining dyes showed a noticeable dulling or color change when dyed in the presence of one or more of the three metal ions. This effect was generally overcome when Agent #1 was present.

There were a few dyes which were adversely affected by the presence of Agent #1. Among these was Calcocid Green B (CI 5) which suffered a severe shade change when Agent #1 was added to the dyebath because it has iron in its structure, which Agent #1 removed. Oxalic acid also had the same effect and, therefore, sequestrants should not be used when dyeing Calcocid Green B.

During studies with the Microdyeoscope, it was observed *(13)* that a number of acid and milling dyes were precipitated by the addition of metal salts. This precipitation was prevented or greatly reduced when Agent #1 was present. Polar Red RS Conc (CI 430) and Calcocid Fast Black 2B (CI 307) are used as examples to show the effect of metal ions on certain milling dyes when applied by Method #4 (see Appendix). These dyes were adversely affected when dyed in the presence of 5 ppm of aluminum ions as shown by a scum on the sides of the beaker and a colored precipitate in the exhausted dyebath. The fastness to crocking was also reduced. Complete protection from aluminum ions was obtained when 3% of Agent #1 was added to the dyebath prior to the addition of the aluminum salt. A duplicate experiment to which 5 ppm of calcium or magnesium ions were added without the presence of Agent #1 did not cause a detectable precipitate or a reduction in fastness properties.

The addition of Agent #1 and the omission of trace metal ions tends to produce dyeings whose shades are similar or slightly brighter than that of the control. The results of some of these tests are listed in Tables VIII and IX.

TABLE I

Dyestuff	*Control*	*+ 2% Agent #1*
Calcofast Wool Orange RN	level from fiber to fiber	marked unlevelness from fiber to fiber
Calcofast Wool Blue BN	bright blue—practically level	dull blue with reddish cast—markedly unlevel
Calcofast Wool Violet 6R	bright violet—practically level	dull, reddish violet, very unlevel from fiber to fiber
Calcofast Wool Green BS	level from fiber to fiber, shade is green	fibers appear gray, level from fiber to fiber
Calcofast Wool Brown GM	level from fiber to fiber	redder, duller, unlevel

EFFECT OF METAL IONS AND AGENT #1 ON METALIZED DYEINGS ———Dye-metal complexes, such as the Calcofast dyes, vary considerably in their resistance to demetalization. In many cases, the affinity for metal of chelate-forming compounds, such as Agent #1, is greater than that of the molecule itself; hence, demetalization of the dye occurs with change in shade.

A group of Calcofast wool dyes was tested by the same general procedure used in the preceding section with acid and milling colors. (See Appendix, Application Method #6). The metal ions usually dulled the shade slightly, but radical shade changes rarely occurred *(15)*. This is probably due to the fact that metalized dyes are produced by reacting the dye with chromium ions to form a stable chromium-dye complex during their manufacture, and the metal is not easily displaced by other metal ions.

The addition of an excess of Agent #1, ie, 2% to a dyebath containing a pre-metalized type of dye in the absence of metal ions, causes a marked and undesirable shade change to occur with about 80% of the metalized dyes tested. These shade changes are brought about by a chemical reaction between Agent #1 and the chromium in the dye-metal complex indicating that the Agent #1-chrome complex is more stable than the dye-chrome complex, under the experimental conditions used. Blues and greens are especially sensitive to sequestering agents, although marked shade changes are obtained with other metalized dyes. Calcofast Wool Green BS is especially sensitive to Agent #1, which demetalizes the dye and destroys the shade. When demetalization occurs, the fastness properties of a dye may also be reduced.

Microscopical examination of cross sections of 2% dyeings of several Calcofast wool dyes made with and without 2% of Agent #1 are shown in Table I.

When it is necessary to use a sequestrant in the application of this class of metalized dyes to control the effect of extraneous metals, the amount of Agent #1 should be reduced to the minimum required to chelate the undesirable metal ions which are present. Any excess above this amount may cause an undesirable change in shade and fastness of the dye. Table II shows the effect on fastness when excessive amounts of Agent #1 were used. Table X shows the effect on shade caused by metal ions in the presence and absence of Agent #1 in the dyebath.

A few of the newer neutral-dyeing metalized dyes were dyed in the presence of different quantities of Agent #1 and none of them were adversely affected as to shade, levelness or fastness properties. In other words, the neutral-dyeing colors give up their metal less easily than the acid metalized dyes, under their respective conditions of dyeing. This is not surprising, since they are dyed at a much higher pH which would be expected to aid the dye in its competition with Agent #1 for the metal.

EFFECT OF METAL IONS AND AGENT #1 ON CHROME DYES——— Chromable dyes generally exhibit the greatest sensitivity to traces of metals because they react readily to form metal complexes, and usually have different shades and fastness properties from those of the unmetalized dyes. The extent of shade change which occurs will be proportional to the amount of metal ions present in the bath and the depth of shade being dyed. The lighter the shade, the greater the shade change will be with the same amount of metal ions.

Sequestering agents are not equally effective with all chrome dyes. To be of practical value in the application of chrome dyes, a sequestering agent must be capable of eliminating or minimizing the effect of traces of aluminum, iron, copper, manganese and nickel ions when the dyes are applied by any of the three common methods———top, meta or bottom chrome. Hydroxylammonium sulfate, the acid sulfate and the chloride were also investigated for possible use as sequestrants because our earlier work had shown that these hydroxylammonium salts prevent or retard the subsequent chromation of certain dyes. The present investigation showed, however, that these salts do not prevent the dye from reacting with the undesirable metal ions; therefore, they could not be used as general-purpose sequestrants.

Tartaric, oxalic and citric acids were found to sequester traces of metal ions; but these acids often have such avidity for chromium ions that chrome dyes are demetalized. These organic acids prevent the formation of the desired chromium complex when bichromate is added to the dyebath for top chroming.

In contrast to the compounds described above, Agent #1 was found to be quite effective as a sequestering agent in the application of chrome dyes. This sequestrant prevented the undesirable metal ions from adversely affecting the shades of a greater number of chrome dyes than any other agent studied. However, its effectiveness varied considerably with different dyes and with different metals on the same dyes.

Since the top-chrome method is used at present to a greater extent by the woolen industry than either the meta or bottom chrome processes, studies on this method are reported in detail. Experiments have shown that Agent #1 will adversely affect the shade of some chrome dyes and definitely improve others. A few of the experiments, using Application Method No. 7 (see Appendix) with and without bichromate, are described to show the wide variations found with different dyes, metal ions and amounts of sequestrant.

For example, 2% dyeings of Calcochrome Fast Red ECB (CI 652) were carried out in the presence of different amounts of Agent #1 in the absence of metal ions. The results are given in Table III.

Other Calcochrome Red ECB dyeings made without Agent #1 in a bath containing 2 ppm of aluminum ions produced a deep, rich shade, much heavier and brighter than a control dyeing made omitting the aluminum ions. Two ppm of copper produced a dyeing which was slightly heavier and yellower than the control. However, the addition of Agent #1 to the baths containing aluminum and copper ions produced weaker dyeings. When 2 ppm of iron was used without Agent #1, the shade was heavier, duller, and browner than the control. The addition of 2% Agent #1 to a similar dyebath containing 2 ppm of iron produced a shade similar to that of the control.

CALCOCHROME FAST BLUE BG ———In contrast to Calcochrome Red ECB, the addition of Agent #1 to 2% dyeings of Calcochrome Fast Blue BG (Pr 93) gave almost complete protection against 2 ppm of aluminum, copper and iron. A comparison of dyeings made with and without the addition of Agent #1 showed the unchromed control dyeing to be duller and bluer. When chromed, the dyeing made with Agent #1 in the dyebath was slightly brighter and greener than the control. Two ppm of aluminum, copper, and iron produced shades which, when chromed and compared with the control, were duller and redder, much redder, and much duller and grayer, respectively. The addition of 2% Agent #1 practically eliminated the adverse effect of the metals on Calcochrome Fast Blue BG dyeings, as is shown by the spectrophotometric reflectance curves in Figures 7 and 8. Figure 7 shows the effect on the dyeing without Agent #1 caused by the presence of aluminum, copper and iron respectively, as compared to the control made without metals. Figure 8 shows the protective action obtained by the addition of 2% Agent #1. Curves D, F, and J practically superimpose on one another, while curve H shows that the dyeing to which copper was added was slightly duller and heavier. The effect of copper is not entirely eliminated by the use of Agent #1.

CALCOCHROME BLUE BLACK CONC ———Two percent dyeings of Calcochrome Blue Black Conc (CI 202) applied as an acid dye, were made with an addition of 2 ppm of aluminum, copper

TABLE II

EFFECT OF 2% AGENT #1 ON FASTNESS PROPERTIES OF CALCOFAST WOOL DYES

	2% Calcofast Wool Yellow N		*2% Calcofast Wool Yellow R*		*2% Calcofast Wool Orange RN*	
	Control	*+ 2% Agent #1*	*Control*	*+ 2% Agent #1*	*Control*	*+ 2% Agent #1*
Light	7	7	6-7	5-6	5-6	5-6
AATCC Wool Wash Test #2						
Shade Change	4	3	4-5	4-5	3-4	3-4
Staining—						
Wool	5	5	5	5	5-	5-
Cotton	5	5	5	5	5-	5-
Silk	5	5	5	5	5-	5-
Viscose	5	5	5	5	5	5
Acetate	5	5	5	5	5	5
Nylon	5	5	5	5	5	5
Alkaline Perspiration						
Shade Change	4	4	4-5	4-5	4	4
Staining—						
Wool	4-5	3	4-5	4	4-5	4
Cotton	4-5	3	4-5	4	4-5	4-5
Silk	4	3	4	3-4	4	3
Viscose	4-5	3	5-	4-5	4-5	4-5
Acetate	5	5	5	5	5	5
Nylon	5	5	5	5	5	5

	2% Calcofast Wool Pink N		*2% Calcofast Wool Bordeaux RB Conc*		*2% Calcofast Wool Bordeaux BN*	
	Control	*+ 2% Agent #1*	*Control*	*+ 2% Agent #1*	*Control*	*+ 2% Agent #1*
Light	6-7	5-6	6-7	6-7	6	6
AATCC Wool Wash Test #2						
Shade Change	4	3	4	4	4	4
Staining—						
Wool	5	5-	4-5	4-5	5	5
Cotton	5	5	5	5	5	5
Silk	5	5	4-5	4-5	5	5
Viscose	5	5	5	5	5	5
Acetate	5	5	5	5	5	5
Nylon	5	5	5	5	5	5
Alkaline Perspiration						
Shade Change	4	4	4	4	4	4
Staining—						
Wool	5-	4-5	4-5	4	5-	5-
Cotton	5-	4-5	4-5	4	5-	5-
Silk	4-5	4	3-4	3	4-5	4-5
Viscose	5-	4-5	4-5	4	5	5
Acetate	5	5	5	5	5	5
Nylon	5	5	5	4-5	5	5

	2% Calcofast Wool Violet 6R		*2% Calcofast Wool Brown GM*		*2% Calcofast Wool Blue R Conc*	
	Control	*+ 2% Agent #1*	*Control*	*+ 2% Agent #1*	*Control*	*+ 2% Agent #1*
Light	6	5	6	6	5-6	5
AATCC Wool Wash Test #2						
Shade Change	2-3	1-2	3-4	2	4-5	2
Staining—						
Wool	5	5	5	5	4-5	4-5
Cotton	5	5	5-	4-5	5	4-5
Silk	5	5	5	5	4-5	4-5
Viscose	5	5	5	5	5	5
Acetate	5	5	5	5	5	5
Nylon	5	5	5	5	5	5
Alkaline Perspiration						
Shade Change	3	2	2	2	4-5	2
Staining—						
Wool	4-5	3	4-5	4	4	3-4
Cotton	4-5	3	4-5	4	4	3
Silk	4	3	4	3-4	3-4	3
Viscose	4-5	3	5	4	4	3
Acetate	5	5	5	5-	5	5
Nylon	5	4	4-5	4-5	5	4

	2% Calcofast Wool Blue BN	
	Control	*+ 2% Agent #1*
Light	5-6	5
AATCC Wool Wash Test #2		
Shade Change	4	5
Staining—		
Wool	5-	5-
Cotton	5-	5
Silk	5	4-5
Viscose	5	5
Acetate	5	5
Nylon	5	5
Alkaline Perspiration		
Shade Change	5	3
Staining—		
Wool	4-5	4-5
Cotton	4-5	4-5
Silk	4-5	4-
Viscose	4-5	4-5
Acetate	5-	5-
Nylon	5-	5

and iron ions. The shade was much redder and brighter than the control when metalized with aluminum, much redder with copper, and much duller and redder with iron. Even when these dyeings were top chromed, the adverse effect on the shade produced by each metal persisted. An addition to the dyebath of 2% Agent #1 did not prevent undesirable shade changes caused by traces of these metals.

CALCOCHROME ALIZARINE RED SC——Similarly, unchromed dyeings of Calcochrome Alizarine Red SC (CI 1034) showed definite color changes when applied in the presence of traces of aluminum, copper and iron. The aluminum complex of Red SC is a bright, yellowish-scarlet, the copper complex, a bluish red, and that of iron, a dull violet. In all cases, the addition of 2% Agent #1 to the dyebaths containing these metals eliminated or minimized their adverse effect on the shade.

TABLE III
CALCOCHROME FAST RED ECB

% Agent #1 in Bath	Unchromed	Chromed
0.0	Control	Control
0.25	sl yellower, sl fuller	sl yellower, sl fuller
0.5	yellower	sl weaker
1.0	yellower & sl weaker	weaker and duller
2.0	yellower, sl weaker and less level	much weaker, duller and yellower

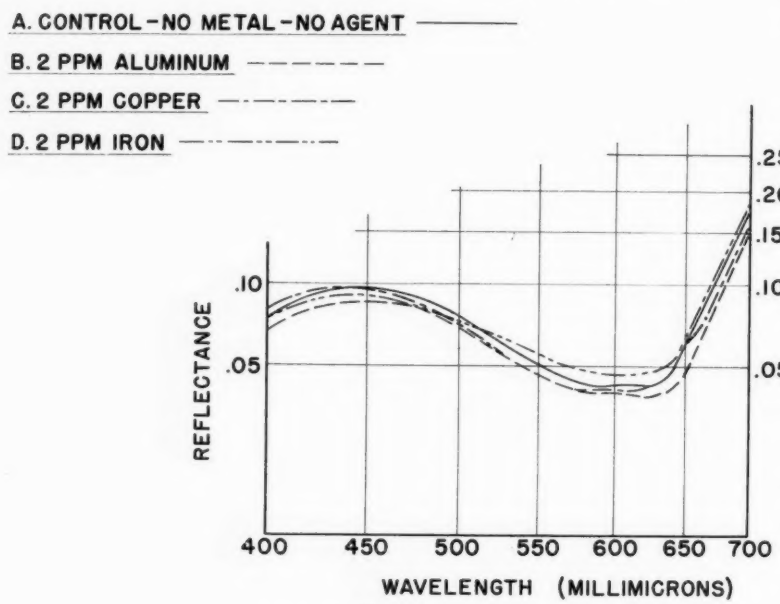


Figure 7
2% Calcochrome Fast Blue BG

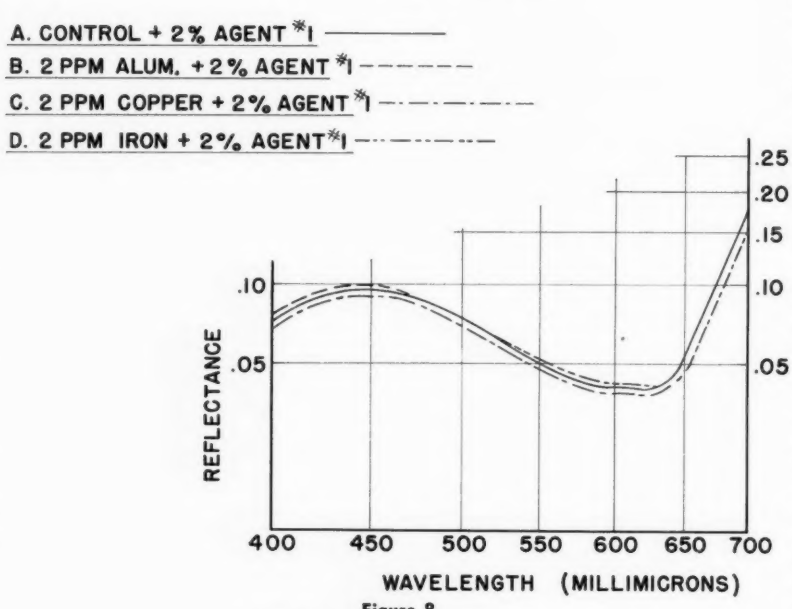


Figure 8
2% Calcochrome Fast Blue BG

CALCOCHROME BLUE BLACK BC AND BLACK T CONC——Calcochrome Blue Black BC (CI 201) and Calcochrome Black T Extra Conc (CI 203) showed unexpected improvement when dyed in the presence of 2% Agent #1 without any unwanted metals being present. The unchromed dyeings were much darker than similar dyeings made without Agent #1. Afterchromed dyeings retained the improvement, being nearly double the strength shown by the control. The effects of trace metal ions on the shade were not overcome entirely; but the increase in strength was maintained and brighter shades were obtained with both blacks when Agent #1 was used.

CALCOCHROME BRILLIANT BLUE BBG——A number of metals, including aluminum, are known to form insoluble lakes by reaction with dyes. This reaction can also occur with dyeings made in the presence of the aforementioned metal ions. These color lakes gradually decompose during the dyeing operation and the amount of original lake is reduced. However, a large proportion of the precipitated lake remains unchanged. Microdyeoscopic studies have shown that some of the lake becomes attached to the fibers and is not removed by repeated rinsing. For example, dyeings of Calcochrome Brilliant Blue BBG (CI 720) made in the presence of 5 ppm of aluminum ions exhibited a heavy blue scum on the sides of the dye beakers. When the dyeing and top-chroming processes were completed, the exhausted dyebath contained a heavy blue precipitate, which settled to the bottom when agitation ceased. (See Figure 9). The dyed wool yielded wet and dry crocks which were much heavier than the control. The depth of shade was also weaker when the aluminum ions were absent from the dyeing. A similar dyeing containing 5 ppm of aluminum plus 2% of Agent #1 was free from scum and precipitate. (See Figure 9). The wet and dry crocks were equal to those of the control, while the shade was brighter and only slightly weaker than the dyeing which did not contain the metal ions and Agent #1.

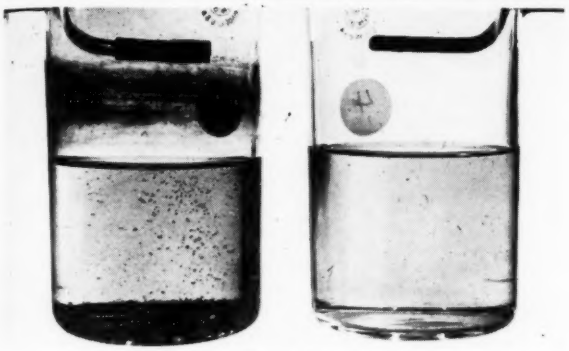


Figure 9

Dyebaths showing effect of aluminum ions with and without Sequestering Agent #1

Dyeing made in beaker at left had an addition of 5 ppm of aluminum ions. Note scum on sides of beaker and flocculent precipitate of the aluminum lake of Brilliant Blue BBG floating in dyebath and at bottom of beaker. Scum and precipitate are a deep blue. Dyeing made in beaker at right had an addition of 5 ppm of aluminum ions and 2% of Agent #1. Note absence of scum and precipitate.

Dyeing Method

2% Calcochrome Brilliant Blue BBG
10% Calcined Glauber's salt
5% acetic acid 28%
Bring to the boil in 30 minutes
Boil one hour, add:
1% sodium bichromate
Boil 45 minutes

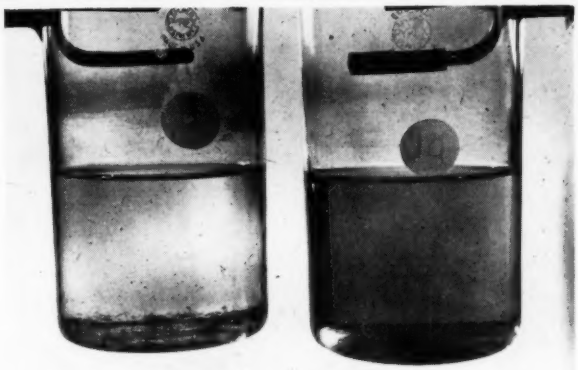


Figure 10

Dyeing made in beaker at left had an addition of 5 ppm magnesium ions. Notice scum on sides of beaker and precipitate at bottom. Dyeing at right had an addition of 5 ppm of magnesium ions and 2% of Agent #1. Note absence of scum or precipitate.

Dyeing Method

2% Calcochrome Yellow CGW Ex Conc
10% Calcined Glauber's salt
5% acetic acid 28%

CALCOCHROME YELLOW CGW ——Figure 10 shows exhausted dyebaths and appearance of beakers when 2% dyeings of Calcochrome Yellow CGW were dyed in the presence of 2 ppm of magnesium ions with and without 2% of Agent #1. The dyeing made without sequestrant had an insoluble precipitate floating in the dyebath and scum on the sides of the beaker. An addition of 2% Agent #1 prevented precipitation of the dye and the accumulation of scum on the sides of the beaker.

The effect on the shade of chrome dyes of metal ions with and without Agent #1 is shown in Table XI.

AMOUNTS OF AGENT #1 REQUIRED ——From an economical point of view it is important to know the amounts of sequestrant which will be required to inactivate traces of metal ions. Our experiments have shown that the theoretical amount of sequestrant which would be required to deactivate the metal ions completely under ideal conditions does not always afford complete protection with many dyes because the dissociation of the sequestrant-metal complex increases as the pH of the dyebath is lowered. In some instances, the use of ten times the theoretical amount of Agent #1 has not eliminated the adverse effect upon the shade caused by a few parts per million of contaminating metal ions. Therefore, increasing the amount of Agent #1 considerably above theory may, in some cases, fail to produce the expected and desired results.

In a study of this problem, several series of dyeings were made on Australian fleece to determine, if possible, the approximate amount of Agent #1 which would be required to sequester known amounts of metal ions. The results are shown in Table IV.

Further studies using 2% Calcochrome Violet B showed that preferential metalization of the dye in the wool tips could be prevented by adding increasing amounts of sequestrant as the ppm of iron were increased. The results are shown in Table V.

These and many other series of dyeings not described in detail have shown that the amount of Agent #1 required to prevent shade changes and inferior fastness properties varies with the dye, the material, the pH of the dyebath, the liquor ratio and the type and amount of metal ions to be controlled. It is recommended that the amount of Agent #1 required be determined in the laboratory. Dyeings should be made on the fabric to be dyed, with samples of the actual dyes selected for the shade, using dyehouse water main-

TABLE IV

2% CALCOCHROME ALIZARINE RED SC—AUSTRALIAN WOOL FLEECE

	ppm of aluminum	*% Agent #1*	*Shade of Tips Compared to control*	*Shade of Body*
Control	0	0	brownish-red (unmetalized shade)	brownish-red
	1	0	scarlet (metalized shade)	brownish-red
	1	1	brownish-red	brownish-red
	2	1	light scarlet	brownish-red
	3	1	scarlet	brownish-red
	2	2	brownish-red	brownish-red
	3	2	light scarlet	brownish-red
	3	3	brownish-red	brownish-red
	5	4	brownish-red	brownish-red

TABLE V

2% CALCOCHROME VIOLET B——AUSTRALIAN WOOL FLEECE

	ppm of iron	*% Agent #1*	*Shade of tips Compared to control*	*Shade of body*
Control	0	0	scarlet (unmetalized shade)	scarlet
	1	0	brown (metalized shade)	scarlet
	1	1	scarlet	scarlet
	2	0	deep brown	dull scarlet
	2	1	dull scarlet	scarlet
	2	2	scarlet	scarlet
	3	0	brown	brownish-scarlet
	3	2	brownish	brownish-scarlet
	3	3	scarlet—sl dull	scarlet—sl dull
	3	4	scarlet	scarlet
	4	0	deep brown	brownish-scarlet
	4	3	scarlet—sl dull	scarlet—sl dull
	4	4	scarlet	scarlet

tained at the liquor ratio and pH which will simulate actual dyehouse conditions.

STUDIES ON THE EFFECT OF METALS———In practice, metal linings and parts of dyeing machines often produce adverse or unexpected shade changes which are rarely ever traced back to the source of metal. Because Eriochrome Verdone A (CI 292) is very sensitive to a variety of metal ions, this dye was used to determine the effect of metals and the amount of Agent #1 which would provide adequate protection for 1% dyeings made on worsted flannel.

Bronze is an alloy of copper and tin, while brass is an alloy of copper and zinc. Both of these alloys are detrimental in dyeing processes because of their copper content. The copperized shade of Verdone A is a blue. Pieces of bronze and of brass each having a surface area of 25.0 cm^2 were used for different dyeings. This amount of metal in a 60-l bath caused the shade to be considerably bluer than the control dyed in the absence of metal. An addition of 1% of Agent #1 provided complete protection.

A piece of monel metal, an alloy of copper, nickel and iron, having a surface area of approximately 25.0 cm^2, made the shade much bluer, probably because of the dominating effect of the release of nickel ions and a lesser effect by copper. Even stainless steel releases sufficient nickel ions to affect the shade of certain dyes. For instance, stainless steel caused the shade of Eriochrome Verdone A to become bluer. However, the effects of both monel and stainless steel were overcome by the addition of ½% of agent #1. In contrast, Agent #1 afforded only slight protection against copper and iron discs when Calcochrome Blue Black Conc was used.

One-percent dyeings of Alizarine Red SC made in the presence of one-half of an aluminum disc with a surface area of approximately 25.0 cm^2 using concentrations of up to 3.0% of Agent #1 showed some protection, but the effect of the released aluminum ions was apparent in the finished dyeing, the tips of the fibers being slightly scarlet. The dyeings made in the presence of Agent #1 showed more complete exhaustion of the dyebath than the control.

One-percent dyeings of Calcochrome Violet B made in the presence of 25.0 cm^2 of mild steel ASTM Type A245C, showed that 1% of Agent #1 failed to prevent the iron ions from producing the brown shade of the iron-dye complex. No improvement was obtained by increasing the amount of Agent #1 even up to 3%.

The effect of time and temperature was studied during the dyeing of the Violet B series with mild steel. It was noted that, initially, the color of all dyebaths was scarlet. The shade of the dyeing made in the presence of mild steel (A245C) and without Agent #1 changed from scarlet to brown when the temperature of the dyebath reached 120°F. The dyeing containing steel and 1% of Agent #1 turned brown about 5 minutes later than did the control. The time interval for changes in dyeings containing 2 and 3% of Agent #1 was about 5 minutes. This experiment was very revealing since it was not known previously that such large quantities of iron ions entered the dyebath at so low a temperature and during the early stages of the dyeing cycle.

EFFECT OF AGENT #1 ON TIPPY DYEING———Previous reports *(3)* and aforementioned studies in this report have shown that traces of metals are absorbed preferentially by the tips of Australian and other fleece wool fibers. The tips of those fibers are dyed the shade of the metal complex when 1 to 5 ppm of aluminum, copper, iron, cobalt, nickel or other metalic ions are present. In the case of Alizarine Red SC in the presence of aluminum ions, when the dyeings are later top chromed, the tips remain scarlet and the body of the fleece is a bluish-red. When Calcochrome Violet B is dyed in the presence of iron and top chromed, the tips may be brown and the body violet. These undesirable bicolored effects produce skittery or heathery dyeings, which result in a lack of solidity of shade and good fastness.

The effect of metal ions is not reversed when the completed dyeings are boiled with 2% of Agent #1. Tippy effects caused by metals remained unchanged when 2% of Agent #1 was added to the "exhausted" dyebath and boiled for a further 40-minute period, prior to top chroming.

Experiments using Australian fleece, cleaned by extracting with carbon tetrachloride and rinsing in warm water containing 1% of Deceresol ®OT surface-active agent, have shown that a bath containing 2% Calcochrome Violet B with 2% Agent #1 added produced dyeings with brighter tips than that of the control wool dyed where iron was absent. This confirms earlier studies by Race and coworkers and the author, that iron is concentrated in the tips of wool fibers during growth and can produce the iron complex of metalizable dyes *in situ* during dyeing *(3, 17)*. The addition of a sequestrant removes this iron and prevents the formation of the iron complex in the fiber tips; therefore, the shade of the tips is brighter. When Agent #1 is omitted, the tips of the dyed fleece are a dark brown (the shade of the iron complex). (See Figure 11).

When 2% of Agent #1 was added to a 2% dyeing of Calcochrome Brown RH (CI 98) in the presence of 3 ppm of nickel, the sequestrant prevented the metal ion from combining with the dye and thus being absorbed by the tips. Dyeings made with 3 ppm nickel but without Agent #1 had reddish-brown tips (the shade of the nickel complex of Brown RH), in contrast to the body portion, which had the normal orange shade.

Agent #1, however, is not equally effective in preventing tippy dyeing with all dyes on fleece wool; thus, with some dyes it is necessary to increase the amount of Agent #1 to 3 or 4% to obtain results equivalent to those obtained with 2% with other dyes. Two percent of Calcochrome Alizarine Red SC dyed in the presence of 3 ppm of aluminum can be used as an example of a dye which required higher percentages of Agent #1. Fleece wool dyeings made with this dye without the addition of Agent #1 had deep scarlet tips and the body was a light brownish-red. An addition of 1% of Agent #1 at the start of the dyeing operation produced dyeings with light scarlet tips and a heavier maroon on the body portion. Subsequent dyeings to which 2 and 3% of Agent #1 was added had light orange-scarlet and slightly orange-tinted tips, respectively. Conversely, the dyeings containing 4 or 5% of Agent #1 produced tips which were undyed and showed that excess amounts of agent completely reversed the positive or heavily-dyed tip effect to that of a negative or undyed tip effect *(18)*. These negative tip effects are undesirable and are similar to effects secured when excessive amounts of nonionic surface-active leveling agents are used. The body section of these fibers was also heavier and bluer as compared to the control dyeing.

Similarly, 2% dyeings of Eriochrome Verdone A made on fleece wool in the presence of 2 ppm cobalt ion had tips which were deep bluish-black with a purple body. An addition of 1, 2 and 3% of Agent #1 progressively reduced the amount of dye in the tips so that the dyeings made with 3% of agent had only a bluish tint. Again an excess of the agent, a 5% addition, yielded dyeings whose tips were practically colorless, while the body was the same shade as the control dyeings made in the absence of cobalt and sequestrant. (See Figure 12).

The foregoing experiments show that, when sufficient quantities of Agent #1 are added to the dyebath, this compound can eliminate or greatly reduce many tippy effects which are caused by preferential absorption of metal ions or their metal-dye complexes. Care must be exercised, however, to avoid the use of excessive quantities of Agent #1 which can prevent the absorption of dye by the tips of the wool fibers.

Figure 11

Wool staples illustrating effect of iron and sequestering Agent #1 on tippy dyeing using 2% Calcochrome Violet B.

Staples from Australian Fleece

A. Control—no metal or Agent #1 added. This staple had dark brownish tips caused by the presence of iron concentrated in this area during growth. All other parts are scarlet.
B. 2 ppm of iron ions added. Tips are brown, body areas are brownish-red.
C. 2 ppm of iron ions and 2% Agent #1 added. Tips and all other areas of staple are a uniform shade of scarlet.

Dyeing Method

3% Calcochrome Violet B
10% Calcined Glauber's salt
5% acetic acid 28%
Brought to boil in 30 minutes and boiled one hour.

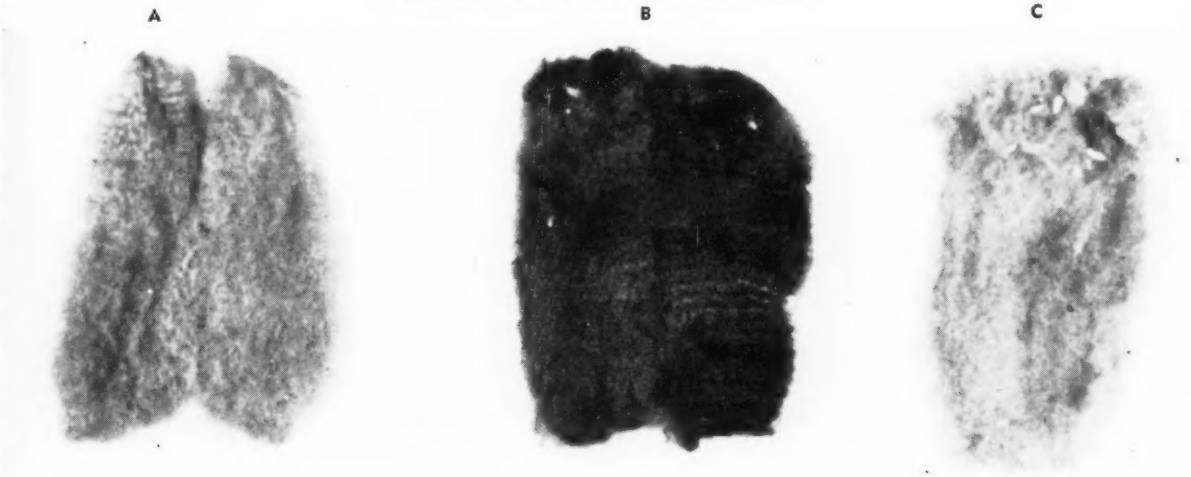


Figure 12

Wool staples illustrating effect of cobalt and sequestering Agent #1 on tippy dyeing using 2% Eriochrome Verdone A.

Staples from Australian Fleece

A. Control—no metal or Agent #1 added. Shade a dull violet.
B. 2 ppm of cobalt ions added. Staple is predominantly blue (the color of the cobalt complex of Verdone A) with reddish body ends.
C. 2 ppm of cobalt ions and 2% Agent #1 added. Staples A and C are similar shade of dull violet and show the sequestering and protective action of Agent #1.

Dyeing Method

2% Eriochrome Verdone A
10% Calcined Glauber's salt
8% ammonium sulfate
Brought to boil in 45 minutes and boiled 1 hour.

TABLE VI

PERCENT OF METALS IN TEXTILE FIBERS AFTER VARIOUS TREATMENTS

	1% Calcomine Brown BN (CI 423) 20% CP sodium sulfate	*1% Calcodur Orange GL Conc (CI 653) 20% CP sodium sulfate*
Cotton boiled out only	0.0012% copper	0.0012% copper
Dyed only	0.0023% copper	0.0028% copper
+ 2 ppm copper	0.0083% copper	0.0113% copper
+ 2 ppm copper + 2% Agent #1	0.0020% copper	0.0018% copper
Cotton boiled out only	less than 0.0001% manganese	less than 0.0001% manganese
Dyed only	less than 0.0003% manganese	less than 0.0003% manganese
+ 2 ppm manganese	0.0019% manganese	0.0022% manganese
+ 2 ppm manganese + 1% Agent #1	less than 0.0003% manganese	less than 0.0003% manganese
Cotton boiled out only	0.0029% iron	0.0029% iron
Dyed only	0.0034% iron	0.0032% iron
+ 2 ppm iron	0.0052% iron	0.0170% iron
+ 2 ppm iron + 2% Agent #1	0.0034% iron	0.0027% iron

TABLE VII

COPPER AND MANGANESE ANALYSIS OF DYE AND TEXTILE FIBER

	Copper	*Manganese*
	(%)	*(%)*
Calcomine Scarlet 4BSY (*CI* 327)	0.0180*	less than 0.0003*
Cotton yarn boiled only	0.0012	less than 0.0001
Cotton dyed with 1% Scarlet 4BSY	0.0059	less than 0.0003
Cotton dyed with 1% Scarlet 4BSY + 2% Agent #1	0.0026	less than 0.0003
Cotton dyed with 1% Scarlet 4BSY + 3% Agent #1	0.0025	less than 0.0003
Calcomine Diazo Rubine BD Conc	0.0065*	0.0031*
Cotton dyed with 2% Diazo Rubine BD Conc Diaz and Dev BN	0.0052	less than 0.0003
Cotton dyed with 2% Diazo Rubine BD Conc + 2% Agent #1, Diaz and Dev BN	0.0044	less than 0.0003
Cotton dyed with 2% Diazo Rubine BD Conc + 3% Agent #1, Diaz and Dev BN	0.0042	less than 0.0003
Calcocid Alizarine Blue SKY (*CI* 1088)	0.0185*	0.0006*
Wool yarn scoured and rinsed only	0.0060	less than 0.0003
Wool dyed with 1% Alizarine Blue SKY	0.0051	less than 0.0003
Wool dyed with 1% Alizarine Blue SKY + 2% Agent #1	0.0013	less than 0.0003
Wool dyed with 1% Alizarine Blue SKY + 3% Agent #1	0.0011	less than 0.0003
Calcosyn Alizarine Sapphire Blue 2GS Conc	0.1320*	0.0002*
Bright acetate fabric scoured and rinsed only	0.0005	less than 0.0001
Acetate dyed with 1% Blue 2GS	0.0007	less than 0.0001
Acetate dyed with 1% Blue 2GS + 2% Agent #1	0.0005	less than 0.0001
Acetate dyed with 1% Blue 2GS + 3% Agent #1	0.0004	less than 0.0001
Calcosyn Red GG Ex Conc	0.0014*	0.0041*
Acetate dyed with 1% Red GG Ex Conc	0.0004	less than 0.0003
Acetate dyed with 1% Red GG Ex Conc + 2% Agent #1	0.0004	less than 0.0003
Acetate dyed with 1% Red GG Ex Conc + 3% Agent #1	0.0004	less than 0.0003

* Based on weight of dye

EFFECTS OF METAL IONS AND AGENT #1 ON DIRECT DYES——— Practical experience has shown that the shade and working properties of many direct dyes are changed by the presence of traces of aluminum, calcium, copper, iron, magnesium and manganese ions. During spectrophotometric measurements of dyes, Stearns *(12)* found that the use of Benzo Fast Yellow 5GL (CI 346) as a test for copper was 40 times more sensitive at pH 9.0, temperature 23°C, than the carbamate method. Thus, the effect of 0.001 milligram per liter of cupric ion added to a 30 milligrams-per-liter solution of Benzo Fast Yellow 5GL can be detected spectrophotometrically.

Such sensitivity of certain direct dyes to metal ions can cause changes which prevent reproducibility of shade from batch to batch. The present series of studies have shown that the shades of many direct dyes applied to cotton and other cellulosic fibers by Methods 8 and 9 (see Appendix) are adversely affected by the presence in the dyebath of a few parts per million of certain metal ions. Additions of Agent #1 generally prevent these adverse effects by sequestering the metal ions. Aluminum, copper and iron ions cause shade changes ranging from heavier and brighter to much duller and weaker. For example, a dyebath containing Calcodur Yellow NN Conc (CI 814) and a trace of copper ions gives a shade heavier and brighter than a standard dyeing not containing copper ions. However, Calcomine Green BY (CI 593) yields a shade much duller and yellower when copper ions are present; Calcomine Red FC (CI 419) is duller and browner when iron is present.

Most of the direct dyes tested exhibited a slight-to-considerable sensitivity to one or more of the usual contaminating metal ions that are to be found in mill waters. By adding 1% of Agent #1 to the dyebath before the addition of the dye, adverse effects of traces of metal ions can be minimized or eliminated. Such protection is to be desired when maximum brightness and trueness of shade is required.

Premetalized direct dyes, like metalized wool dyes, were generally affected to a lesser extent by the presence of metal ions though slight color changes were observed. These improved direct dyes contain the metal as part of the dye molecule, and are therefore less liable to react with contaminating metal ions. When 2% of Agent #1 was added to baths containing some of the metalized directs, ie, Calcodur Violet 4RL, the metal was removed from the dye molecule, resulting in radical and undesirable color changes accompanied by a reduction in fastness properties. Since contaminating metal ions in dyebath waters affect the shades of metalized direct dyes only slightly, it is recommended that sequestrants be eliminated or reduced to a minimum when applying metalized direct dyes. The effect on shade of metal ions on direct and developed dyes with and without Agent #1 is shown in Tables XII and XIII.

USE OF AGENT #1 IN DYEING COTTON TO BE RUBBERIZED——— Cotton and rayon materials for bath mats, throw rugs, carpets, automotive carpets and fabrics where the back is rubberized should be dyed, as far as possible, in the absence of copper and manganese. Textile trade specifications for rubberized materials have been established which usually limit the permissible amount of copper to 0.001% and that of manganese to

TABLE VIII

ACID DYES—EFFECT ON SHADE

Dye	CI No.	Method	Normal shade	+1% Agent #1	+2 ppm aluminum		+2 ppm copper		+2 ppm iron	
					No agent	+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1
Calcocid Fast Yellow 3G Ex Conc	636	1	bright yellow	similar	similar	similar	similar	similar	similar	similar
Calcocid Fast Yellow 2G	639	2	light yellow	similar	similar	similar	similar	similar	similar	similar
Calcocid Yellow MCG	640	1	yellow	similar	similar	similar	SD	SR & S Br	VSG	similar
Calcocid Yellow S	10	1	deep yellow	SR & S Br	SR	SR & S Br	SD	SR & S Br	SR & VSD	VSR
Calcocid Fast Light Orange 2G	27	1	orange	similar	SW	similar	similar	similar	VSD	similar
Calcocid Orange Y Ex Conc	151	1	bright orange	similar	VSY	similar	VSY & D	similar	VSD	similar
Calcocid Orange RR	161	1	rich red-orange	similar	similar	similar	SD	similar	SR & VSD	SR
Calcocid Eosine G	114	1	bright red	VSW & D	VSW & D	similar	VSD	similar	VSD	similar
Calcocid Phloxine 2G	31	1	light red	similar	SW & B	VSW	SW & D	similar	VSW & D	VSW
Calcocid Fast Red BL Pr	101	2	clear red	similar	similar	similar	VSW & D	similar	VSD	similar
Calcocid Alizarine Red RR	1091	3	light red	similar	VSD	similar	SD	similar	SB & D	similar
Calcocid Fuchsine 6B	57	1	deep blue-red	similar	VSD	similar	VSD	similar	VSD	similar
Calcocid Scarlet 2R	79	3	light orange-red	MW	similar	MW	SD	similar	W	MW
Calcocid Brilliant Scarlet 3RN Conc	185	3	lt bluish-red	SH	H	MW	BW & D	similar	SH	MW
Calcocid Fast Red A	176	1	rich red	SW & VSY	SW	similar	SW & SD	similar	VSD	similar
Calcocid Rubine XX Conc	179	1	deep blue-red	similar	similar	similar	VSD	similar	VSD & B	VSW
Calcocid Scarlet MOON	252	3	scarlet	similar	VSY	similar	VSD	similar	VSD & B	similar
Calcocid Fast Violet R	758	3	red-violet	similar	VSD	similar	VSD	similar	VSD & B	similar
Calcocid Alizarine Violet NC	1080	3	dull blue-violet	similar	VSR	similar	SD	similar	VSD & B	similar
Calcocid Fast Violet 3R		1	blue-violet	similar	VSB & D	similar	VSD	similar	similar	similar
Calcocid Fast Violet 2R Conc Pr	197	1	dull red-violet	similar	VSR	similar	SD	similar	VSD	similar
Calcocid Violet 4BXN	698	2	br violet	similar	similar	similar	SD	similar	VSD	similar
Calcocid Fast Violet BG Conc	699	1	royal blue	similar	similar	similar	VSD	similar	similar	similar
Calcocid Alizarine Blue SKY	1088	3	light blue	similar	similar	similar	similar	similar	VSG	similar
Calcocid Alizarine Blue SE	1053	1	light blue	similar	similar	similar	VSD	similar	similar	similar
Calcocid Alizarine Blue SAPX	1054	1	deep, red-blue	SH & VSR	SW & VSG	similar	SG & SD	similar	VSD	similar
Calcocid Alizarine Blue SAPG	1054	1	light blue	similar	similar	similar	VSD	similar	VSD	similar
Calcocid Alizarine Blue A2G Pr	10	2	light blue	similar	similar	similar	SD	similar	similar	similar
Calcocid Alizarine Blue SBA Pr	12	3	deep blue	similar	SH & S Br	similar	SG & SD	similar	SG & SD	similar
Calcocid Fast Blue BL	833	3	medium blue	similar	similar	similar	VSD	similar	similar	similar
Calcocid Fast Blue GL	833	3	medium blue	similar	similar	similar	VSD	similar	VSD	similar
Calcocid Blue AX Double	714	1	bright blue-green	similar	similar	similar	VSD	similar	similar	similar
Calcocid Blue EG	671	1	deep, bright, greenish blue	SW & VS Br	similar	SW & VS Br	MG & VSD	SW & VS Br	SG & VSD	SW & VSD
Calcocid Green SB Ex Conc	737	1	blue-green	similar	VSB	similar	VSG	similar	similar	similar
Calcocid Green S Ex Conc	737	1	medium bluish-green	SW	similar	SW	SY & SD	SW	similar	similar
Calcocid Green G Conc	666	3	deep yellowish-green	SH	SY & S Br	SY & S Br	SH & SY	similar	VSY & VSD	similar
Calcocid Green B Conc	5	3	olive green	MW & D	similar	MW	SW	VW & D	VSW	VW & D
Calcocid Blue Black 2R Ex Conc	246	3	dull green-blue	similar	SH	similar	similar	similar	SD	similar
Calcocid Blue Black Ex Conc	246	3	dull green-blue	similar	similar	similar	similar	similar	similar	similar

TABLE IX

MILLING DYES—EFFECT ON SHADE

Dye	CI No.	Method	Normal shade	+1% Agent #1	+2 ppm aluminum		+2 ppm copper		+2 ppm iron	
					No agent	+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1
Calcocid Milling Yellow 5GC Conc	642	4	clear yellow	similar	similar	similar	SD	similar	VSD	similar
Calcocid Milling Yellow 3G	642	4	clear yellow	similar	VSD	similar	SD	similar	VSD	similar
Calcocid Milling Yellow R Pr	187	4	bright yellow	S Br	similar	S Br	SW	S Br	SD	S Br
Calcocid Milling Orange GSC Conc Pr	151	4	light orange	VS Br	VS Br	VS Br	VSD	VS Br	VSD	VS Br
Calcocid Milling Orange 4R Conc		4	medium orange	similar	VSD	similar	SW & D	similar	SD	similar
Calcocid Milling Red G	443	4	orange-red	similar	similar	similar	VSD	similar	VSD	similar
Calcocid Milling Red GP Conc	430	4	scarlet	similar	VSD	similar	similar	similar	VSD	similar
Calcocid Milling Red 3R Conc	275	4	bright red	similar	similar	similar	similar	similar	similar	similar
Calcocid Milling RED RC Conc	430	4	bright red	similar	similar	similar	VSD	similar	similar	similar
Calcocid Milling Red 3B	487	4	bright red	similar	similar	similar	VSD	similar	similar	similar
Calcocid Milling Red RS Conc	430	4	bright red	similar	SD & W	similar	VSD	similar	VSD	similar
Calcocid Milling Red 7B Conc	430	4	claret	similar	W & B	similar	SB & SD	similar	SW & SB	similar
Calcocid Brilliant Blue FFR Ex Pr	40	4	bright blue	similar	VSD	similar	VSD	similar	VSD	similar
Calcocid Milling Blue BC Pr	37	4	medium dull blue	similar	VSD	similar	SD	similar	VSD	similar
Calcocid Wool Blue B Conc	707	4	medium dull blue	similar	H	similar	H, SD uneven	similar	H	similar
Calcocid Fast Blue SR	208	4	dull blue	similar	H	similar	W, skittery	similar	VSD	similar
Calcocid Navy Blue 2G	288	5	medium blue	similar	similar	similar	VSG	VSD & G	similar	VSD & G
Calcocid Navy Blue 3R Conc	289	5	navy blue	VSD	similar	VSD & G	VSD	similar	VSD	similar
Calcocid Milling Green 6B Conc	667	4	blue-green	similar	similar	similar	VSW	similar	similar	similar
Calcocid Milling Fast Green CR	735	4	light green	similar	similar	similar	VSY	similar	similar	similar
Calcocid Alizarine Green CG Ex	1078	4	light green	similar	similar	similar	similar	similar	similar	similar
Calcocid Alizarine Green CGN Ex	1078	4	light green	similar	similar	similar	similar	similar	similar	similar
Calcocid Neutral Black 2B Conc	304	4	blue-black	VSW	similar	similar	similar	similar	VSD	similar
Calcocid Fast Black 2B	307	5	blue-gray	similar	similar	similar	W & D	similar	VSW & D	similar
Calcocid Fast Black B	307	5	dull, blue-gray	similar	similar	similar	VSD	similar	similar	similar

TABLE X

CALCOFAST DYES (METALIZED)—EFFECT ON SHADE

Dye	Pr No.	Method	Normal shade	+1% Agent #1	+2 ppm aluminum		+2 ppm copper		+2 ppm iron	
					No agent	+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1
Calcofast Wool Yellow 8G Conc	——	6	greenish-yellow	VSR	VSD	VSR	SD	VSR	VSD	VSR
Calcofast Wool Yellow N	——	6	medium yellow	SR	similar	SR	SD	SR	VSD	SR
Calcofast Wool Yellow R	Pr 316	6	orange-yellow	SR	VSD	SR	SD	SR	VSD	SR
Calcofast Wool Orange RN	Pr 324	6	medium orange	R	VSD	SR	SD	R	VSD	R
Calcofast Wool Orange 2R	Pr 146	6	bright orange	similar	similar	similar	VSD	similar	VSD	VSY
Calcofast Wool Brown GM	——	6	red-brown	B & D	VSD	B & SD	VSD	B & D	similar	B & D
Calcofast Wool Red GA	Pr 391	6	brick red	VS Br	similar	similar	VSD	VS Br	VSH	VS Br
Calcofast Wool Pink N	Pr 326	6	bright pink	SB	VSD	SB	SD	SB	similar	SB
Calcofast Wool Bordeaux RB Conc	——	6	maroon	D & Brown	similar	D & S browner	similar	D & brown	similar	D & brown
Calcofast Wool Bordeaux BN	——	6	claret	B & D	VSD	B & SD	SD	B & D	VSD	B & D
Calcofast Wool Violet 6R	Pr 329	6	blue-violet	browner	VSD	B & D	VSD	S browner	similar	S browner
Calcofast Wool Blue R Conc	——	6	deep blue	R	VSD	SR	VSD	R	VSD	R
Calcofast Wool Blue BN	Pr 318	6	medium blue	SR & SD	similar	SD	VSW	VSR & SD	similar	VSR & SD
Calcofast Wool Blue 2B	——	6	light blue	R	VSD	SR & D	VSD	SR & D	VSD	SR & D
Calcofast Wool Blue 2G	——	6	greenish-blue	VMR	similar	R	similar	MR	similar	MR
Calcofast Wool Green DKB	——	6	green	SY & SD	VSD	VSY & VSD	SD & B	SD & VSY	VSD	VSD & VSY
Calcofast Wool Green BS	——	6	light green	dull pinkish-gray	similar	greenish-gray	VSD	light bluish-taupe	VSD	gray
Calcofast Wool Black WA	Pr 143	6	black	similar	VSH	similar	VSR	similar	VSH	similar

TABLE XI

CHROME DYES—EFFECT ON SHADE

Dye	CI No.	Method	Unchromed	Chromed	+2% Agent #1		+2 ppm aluminum		+2 ppm copper		+2 ppm iron	
					Unchromed	Chromed	Chromed	+2% Agent #1 Chromed	Chromed	+2% Agent #1 Chromed	Chromed	+2% Agent #1 Chromed
Calcochrome Yellow G	Pr 56	7	weak yellow	strong yellow	similar	similar	similar	similar	SW	VSW	VSD	similar
Calcochrome Yellow 2G	36	7	light yellow	strong greenish yellow	VS Br	similar	VSD	similar	VSD	similar	SD	VSR
Calcochrome Yellow EFA Conc	219	7	creamy yellow	dull orange-yellow	similar	VSR	VSD	similar	SD	similar	SD	VSD & R
Calcochrome Yellow CGW 250%	——	7	light golden yellow	orange-yellow	S Br	similar	SY	similar	VSY & D	similar	VSY & D	similar
Calcochrome Orange GR	274	7	bright golden yellow	red orange	VS Br	VSR	similar	similar	VSD	VSR	similar	similar
Calcochrome Orange LC	——	7	brick red	orange	SR	similar	SD	similar	VSY	similar	D	VSD
Calcochrome Orange R Ex Conc	40	7	bright golden yellow	dull red-orange	similar	VSW	VSD	VSY	SY	VSY	VSY	VSY
Calcochrome Brown EB	Pr 14	7	brownish-red	deep bluish-brown	similar	similar	similar	similar	SY & W	similar	similar	similar
Calcochrome Brown PG	Pr 4	7	dull red	yellowish-brown	sl Br	VSH	VSY	VSH	VSW	similar	VSW & D	VSH
Calcochrome Brown RH	98	7	yellow-orange	warm red-brown	sl Lighter	VSB	VSH	similar	SW	VSW	VSY	similar
Calcochrome Brown 2R	167	7	golden yellow	dull red-brown	similar	similar	VSB	VSW	much W	SW	W	W
Calcochrome Brown ROC	——	7	red	deep brown	Br	Sl H	VSH	VSH	W & Y	VSY	VSW	YSH
Calcochrome Fast Red ECB	652	7	weak dull orange	bluish-red	SY	W	Br & H	W	SH & Y	W	H & D	VSW
Calcochrome Alizarine Red SC	1034	7	dull weak red	strong full red	SW	SH	SW & Y	VSY	VSW	VSD	VSW	VSH
Calcochrome Silk White Red B	216	7	bright orange	medium red	Sl Br	H	SH	SH	SD	SD & H	SD	SD & H
Calcochrome Violet B	169	7	dull red-orange	dark violet	VS Br	VSH	VSR & W	similar	VSW	similar	SD	VSD
Calcochrome Brilliant Blue BBG	720	7	red-brown	bright blue	Br	similar	VSH	similar	similar	similar	VSD	similar
Calcochrome Blue F4B	180	7	bright red	navy	similar	similar	VSB	similar	VSD & R	similar	VSD	similar
Calcochrome Alizarine Blue Black B	1085	7	deep purple	dull purplish black	VSH	VSH	SR	VSH	SR	VSR & H	VSD	VSH
Calcochrome Blue Black R Conc	202	7	maroon	blue-black	VSD	VSW	SR	VSR	R	SR & W	D	SD & W
Calcochrome Blue Black ZF Conc	202	7	maroon	blue-black	SW&redder	similar	SR	VSR	R	SR	D	SD
Calcochrome Blue Black BC	201	7	purple	dull blue	heavier	heavier	redder	stronger	W & R	R	dull gray	D & H
Calcochrome Black T Ex Conc	203	7	purple	greenish-gray	heavier	heavier	hy blue-gray	bluer	SR	R & H	DR & W	H
Calcochrome Black F Conc	299	7	deep purple	greenish-black	similar	similar	VS greener	VS greener	VSR	similar	VSW & D	similar
Calcochrome Alizarine Blue Black 3B	1085	7	violet	blue-gray	VSW	SH	SB & W	SB	similar	VSH	VSD & W	VSH
Calcochrome Black PV Conc	170	7	red-violet	dull blue-black	similar	similar	SW	SH & D	VSR & W	similar	SD & W	SD
Calcochrome Alizarine Gray 2BLS	Pr 206	7	blue-gray	greenish-gray	similar	similar	similar	similar	similar	similar	similar	similar

TABLE XII

DIRECT DYES—EFFECT ON SHADE

TABLE XII

DIRECT DYES—EFFECT ON SHADE

1% Dye	CI No.	Dyeing Method	Normal Shade	2 ppm aluminum		2 ppm copper		2 ppm iron	
				+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1
Calcodur Yellow 4GL	346	8	deep brilliant yellow	VSG	SD	VSG	SR	SG	VSD	similar
Calcodur Yellow NN Conc	814	8	reddish brilliant yellow	SH	VSR	SH	VSR	SH	VSD	SH
Calcodur Yellow BL Conc	814	8	deep reddish yellow	SW	VSD	VS Br	VSD	VSW	VSD	VSW
Calcodur Yellow RL	349A	8	medium reddish yellow	VSG	SR	similar	VSD	similar	SD & SG	similar
Calcomine Brilliant Yellow Conc	365	8	deep brilliant reddish yellow	SR	SW & SG	similar	SG	similar	VSD	VSR
Calcomine Yellow AF	622	8	medium brilliant reddish yellow	similar	VSD	VSR	VSG	VSW & VSR	similar	similar
Calcomine Chinoline Yellow P	802	8	light greenish yellow	similar	similar	similar	SW	similar	SW	similar
Calcomine Brilliant Paper Yellow Conc	364	8	deep brilliant red-yellow	S Br	similar	S Br	similar	S Br	similar	S Br
Calcodur Orange E3GL	——	8	medium dull orange	VSR	VSD	similar	VSD	VSR	SY	VSR
Calcodur Orange EGL	Pr 72	8	medium dull reddish orange	VSR	VSD	VSR	VSY	VSR	SD	VSR
Calcodur Orange GL Conc	653	8	deep brilliant orange	SY	SR & SD	SY	R & D	SY	VD	SY
Calcomine Orange R Special	621	8	medium dull orange	VSY	VSR	VSY	VSR	similar	similar	similar
Calcomine Orange 5RE	621	8	light burnt orange	VSW	VSD	similar	VSD	similar	SD	similar
Calcodur Orange ERL	Pr 73	8	medium dull reddish-orange	similar	similar	similar	VSR	VSR	similar	similar
Calcomine Fast Orange 2RS Conc	326	8	medium brilliant reddish-orange	similar	similar	VSW	similar	similar	similar	similar
Calcomine Silk Orange RN Conc	415	8	deep reddish-orange	SH & S Br	similar	similar	SR & SD	similar	R & MD	SR & D
Calcomine Fast Orange 2R	326	8	medium brilliant red orange	similar	similar	similar	SR & SD	similar	VSR & VSD	SR
Calcomine Yellow Brown K Ex	596	8	deep burnt orange	similar	VSY & VS Br	similar	similar	similar	similar	similar
Calcomine Catechu 4G Conc	Pr 70	8	medium tan	similar	VSR	similar	SR	similar	SR & SD	similar
Calcomine Catechine 3RS	——	8	light reddish brown	MY & M Br	SY & S Br	MY & M Br		MY & M Br	VSY	MY & M Br
Calcomine Brown BN	423	8	deep dull brown	SY	SR	SY	MR	similar	MR	similar
Calcomine Brown M	420	8	medium reddish brown	similar	VSR	similar	VSD	similar	SD	VSW
Calcodur Brown 4RL	——	8	medium brilliant brick red	similar	similar	S Br & SY	S Br & SY	S Br & SY	VSY & VSD	VSY & VS Br
Calcomine Catechu LB Conc	Pr 68	8	medium dull brown	SH & SB	W & MB	SB	MR	similar	H & B	SH & SB
Calcomine Fast Scarlet YA	326	8	medium brilliant yellow red	SH & S Br	SH & S Br	SH & S Br	B & D	SH & S Br.	similar	SH
Calcomine Red 4BX Conc	448	8	deep brilliant red	VSY	similar	similar	VSD	VSY	VSY & VSD	VSY & VSD
Calcomine Scarlet 4BSY	327	8	medium brilliant red	similar	VSW	similar	SD	similar	similar	similar
Calcomine Red FC	419	8	medium dull bluish red	similar	SH & S Br	similar	SD	similar	D	similar
Calcomine Fast Red 8B	——	8	light brilliant bluish red	H	VSH	H	SD	H	SD	H
Calcomine Fast Scarlet 8BC Ex	326	8	medium bluish red	similar	similar	similar	SD	similar	VSD	similar
Calcodur Red 8BL	278	8	medium bluish red	similar	SW	SB & SW	SD & SW	similar	SY	B & D
Calcodur Red 3BL	——	8	medium orchid	similar	VSD	similar	VSD	similar	similar	similar
Calcodur Pink 2BL	353	8	deep bluish pink	similar	similar	similar	VSD	similar	similar	similar
Calcomine Garnet BY Conc	275	8	dull wine	VSB	VSH	similar	SH & D	similar	VSD	H & SD
Calcomine Garnet B	375	8	plum	similar	SY & S Br	SY & S Br	SY	SY & S Br	SY & S Br	VSY
Calcomine Bordeaux 6BN	Pr 67	8	light wine	similar	VSH	similar	SD	similar	similar	similar
Calcomine Brilliant Rubine B	——	8	medium red violet	VSY	SY	SY & S Br	SY & S Br	Y & B	SY & S Br	SY & S Br
Calcomine Scarlet 3B	382	8	medium bluish red	similar	similar	similar	VSD	similar	VSD	VSD
Calcomine Scarlet B	382	8	medium brilliant red	Y & B	VS Br	SB & MY	VSD	VSY & VS Br	VSY	SY & SH
Calcocid Milling Red GP Conc	430	8	light red	similar	similar	similar	MD	similar	H & SY	SH
Calcodur Red 6BL	——	8	medium bluish red	similar	SH & SY	SH & SY	SH & SY	SH & SY	H & Y	SH & Y
Calcomine Fast Scarlet 4BNC	326	8	medium brilliant red	similar	similar	similar	SW, SB & D	similar	similar	similar
Calcodur Violet 4RL	——	8	medium reddish violet	MR	VSD	MR	similar	MR	VSD	MR
Calcomine Brilliant Violet 2R	——	8	brilliant deep violet	VSR & VS Br	VSR&VS Br.	SR	SR	SR	SR	similar
Calcomine Violet N Conc	394	8	deep dull violet	VSH	similar	VSH	SR & SD	VSH	VSD & VSH	VSH
Calcomine Brilliant Violet B Conc	Pr 35	8	deep brilliant bluish violet	similar	VSR & VSD	VSR & VSD	SB & SD	similar	SR & SD	SR
Calcodur Violet 4BL Ex Conc	325	8	deep brilliant bluish violet	SR	SR & S Br	SH & SR	VSR	SH & SR	SR	SR
Calcomine Violet B Conc	387	8	medium dull bluish violet	W & R	SR	SR	R & D	R & D	SR	SR
Calcomine Blue R Conc	515	8	medium reddish blue	similar	similar	similar	SR & VSD	similar	similar	similar
Calcomine Azurine BT Conc	502	8	deep blue	similar	similar	similar	similar	similar	similar	similar
Calcodur Blue SL	Pr 71	8	medium dull blue	similar	VSD	VSD	VSR & SD	VSR & SD	similar	VSR & VSD
Calcomine Blue DR	——	8	light dull reddish blue	VSR	VS Br	VS Br	VSG	VS Br	VSD	VS Br
Calcomine Navy R	——	8	light dull red navy	similar	VSG & VSD	similar	SR & SD	SR	SH & SD	VSR & VSD
Calcomine Blue 2B Ex Conc	406	8	medium brilliant blue	similar	similar	similar	similar	SW & VSR	SR	SW & SR
Calcodur Blue 4GL	533	8	light greenish blue	similar	similar	similar	VSD	similar	VSD	similar
Calcomine Sky Blue EX Conc	520	8	deep greenish blue	similar	similar	similar	VSD	similar	similar	similar
Calcodur Blue 8GL Conc	Pr 27	8	medium dull greenish blue	similar	similar	similar	similar	similar	similar	similar
Calcomine Sky Blue FF Ex Conc	518	8	light blue	similar	similar	similar	VSD	similar	VSD	similar
Calcodur Turquoise GL	Pr 278	8	brilliant turquoise	S brighter	similar	similar	SG & SD	S Br	VS Br	VS Br
Calcomine Green GN Conc	594	8	medium green	VSY	similar	similar	SD	similar	VSD	similar
Calcomine Green BY Conc	593	8	medium dull bluish green	similar	similar	similar	SY & SD	similar	similar	similar
Calcomine Green BT Conc	589	8	medium dull bluish green	similar	SH	similar	VSD	similar	VSD	similar
Calcomine Dark Green BG Conc	583	8	deep bluish green	VS Br	similar	VS Br	SD	VS Br	VSD	VS Br
Calcodur Blue Green BG	Pr 470	8	pale blue green	similar	VSD	similar	VSD	similar	SD	similar
Calcomine Brilliant Green Y	——	8	brilliant medium yellow green	SB	VSD	SB	SY	SB	similar	VSB
Calcomine Green 5GSC	——	8	deep dull yellow green	SW & S Br	similar	SH & S Br	VMD	SH & S Br	VSD	SH & S Br
Calcodur Gray L	Pr 24	8	dull blue gray	VSH	VSH	similar	SH	similar	VSD	similar
Calcomine Fast Black F Conc	539	8	light reddish black	SH & SG	SR	SG & S Br	MR & D	SH & SG	VSG&VS Br	SG & S Br
Calcomine Black 5RE Conc	582	8	light black	similar	similar	similar	SY	similar	similar	similar
Calcomine Black R 200%	582	8	medium reddish black	SH & SG	VSD	SG	MR & D	SH & SG	VSD	SH & SG
Calcomine Black EB 200%	581	8	light black	VSH	similar	VSH	SY	VSH	VSY	VSY
Calcomine Black 200%	581	8	medium reddish black	similar	similar	similar	MD	SD	SD	SH & VSD

TABLE XIII

DEVELOPED DYES—EFFECT ON SHADE

1% Dye	CI No.	Developer	Method	Normal Shade Direct	Normal Shade Developed	+1% Agent #1 Direct	+1% Agent #1 Developed	2 ppm aluminum Direct No agent	2 ppm aluminum Direct +1% Agent #1
Calcomine Diazo Orange RXD	Pr 173	BN	9	deep yellow	light orange	similar	SH	SH	SH
Calcomine Diazo Orange RRD Conc	——	BN	9	med red-orange	medium burnt orange	VS Br & SH	SW	SH & S Br	SH & S Br
Calcomine Diazo Brown 2RD	——	BN	9	light rust	light brick red	similar	similar	similar	SH
Calcomine Diazo Scarlet PRD	812	BN	9	deep yellow	light red	SH	SW	similar	SH
Calcomine Diazo Scarlet RPR Double Conc	Pr 80	BN	9	deep red	deep red	SH	similar	SH	SH
Calcomine Diazo Bright Scarlet ROAD	Pr 80	BN	9	light red	medium bluish red	SY & Br	SH & SY	VSY	SY & Br
Calcomine Diazo Bordeaux D Ex Conc	Pr 77	BN	9	deep red-violet	deep dull red-violet	Y & Br	SY & S Br	SY & S Br	Y & Br
Calcomine Diazo Bordeaux RB Conc	——	BN	9	deep orange	medium dull bluish red	SW	S Br	SW	SW
Calcomine Diazo Blue 2BD	Pr 90	BN	9	light dull reddish blue	light bright red	similar	similar	VSR & VSD	similar
Calcomine Diazo Blue 2RWD Conc	317	BN	9	light reddish navy	deep bright reddish blue	similar	similar	SR & SD	similar
Calcomine Diazo Brilliant Green 3GD	Pr 78	Z	9	bright sky blue	light yellow-green	VSR & VS Br	similar	similar	VSR & VS Br
Calcomine Diazo Green BLD Conc	——	Z	9	medium green blue	medium green	SR & VS Br	similar	VSR & VSD	SR & VS Br
Calcomine Diazo Black BTCW	401	TD	9	medium blue	medium greenish-black	VSH	similar	SD	VSH & VSR
Calcomine Diazo Black OBD	Pr 147	TD	9	light dull blue	light reddish-black	VSH	VSH	VSR	similar
Calcomine Diazo Black VJ Conc	Pr 202	TD	9	deep greenish gray	medium reddish black	VS Br	VS Br	similar	similar

0.0005%. It is known *(14)* that the presence of minute amounts of ionizable copper and manganese may depolymerize raw rubber, making it soft and sticky. Vulcanized and synthetic rubbers are also adversely affected by the presence of certain metal ions because these ions promote oxidation and accelerate aging to such an extent that the rubber loses tensile strength and elasticity, resulting in embrittlement.

Many direct dyes now in general use may contain from "only a trace" to "many parts per million" of copper, manganese and other contaminating metal ions. These contaminates can dull the shade or may be present in sufficient quantities to cause deterioration of the rubber.

We also know that it is possible to color rubber with pigments which contain chelated copper without adversely affecting the properties of the rubber. For example, the copper phthalocyanine blues and greens have been in general use for many years without causing rubber to deteriorate.

During this investigation a large number of tests were made to determine the effect of copperized direct dyes on rubber. The results indicate that damage to rubber occurs when such dyes contain free, ionizable copper. Copper, in the form of a chelated copper-dye complex, had no greater effect upon rubber than the copper-free unmetalized direct dyes used as controls.

Dyers know that certain rubber accelerators demetalize direct dyes and cause shade changes and loss of fastness properties. The accelerator-metal complex may break down and release copper ions during the curing period and adversely affect rubber.

Copperized direct dyes have been used without precautions on many types of fabrics and have not caused deterioration of the rubber backings. It should therefore be possible to prevent copper ions from adversely affecting rubber backings by the addition to the dyebath of small amounts of sequestering or chelating compounds, such as Agent #1. Such compounds will form a soluble sequestrant-copper complex which is readily removed from the dyed materials by rinsing in water.

A large number of dyeings made in the presence of metal ions with and without the addition of Agent #1, and analyzed quantitatively by colorimetric and spectroscopic methods, have shown that detrimental copper and manganese ions can be inactivated by adding this sequestrant to the dyebath. This should simplify the dyer's problem by eliminating the need for copper and manganese-free dyes, which may not be available. It should also be emphasized that dyes are not the only source of detrimental copper and manganese, since these metal ions may come from equipment, ground water, piping and machines. Tables VI and VII show the amounts of metal ions detected by analysis and prove rather conclusively that it is possible to inactivate a considerable portion of the metal ions which are detrimental to rubber.

ACKNOWLEDGMENTS

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REFERENCES

(1) "The Modern Chelating Agent", Bersworth Chemical Company (1949).

(2) Diehl, "The Chelate Rings", *Chem Rev* 21, 39 (1937).

(3) Millson, H E, "Effect of Metals on Tippy Dyeing", *Am Dyestuff Reptr* 38, 378 (1949).

(4) Joerger, Robert W, "Dyeing Wool Stock, Tops and Yarn — Article 4 — Chrome Dyes", *Textile Inds* 114, 125 (1950).

(5) "A Versatile Auxiliary Compound", *Dyer* 101, 81 (1949).

(6) Bird, C L, and Malloy, E J, *J Soc Dyers Colourists* 55, 560 (1939).

(7) *Ibid* 57, 224 (1941).

(8) Grundy, J G, "Some Observations on the Suitability of Various Metals and Alloys for Dyeing Machines", *J Soc Dyers Colourists* 45, 39 (1929).

(9) Grundy, J G, "Further Notes on the Suitability of Metals for Dyeing Machinery", *ibid* 51, 377 (1935).

(10) Miller, L B, "Iron Bacteria in Industrial Process Water", *Rayon Text Monthly* 29, 77 (1948).

(11) Bird, C L, "The Theory and Practice of Wool Dyeing", Enlarged Edition, Soc Dyers and Colourists (1951).

(12) Stearns, E I, "A Dye Extremely Sensitive to Copper", *Ind Eng Chem* 14, 568 (1942).

(13) Millson, H E and Turl, L H, "Microscopical Dyeing Phenomena, Studies with the Microdyeoscope", *Textile Research J* 10, 685 (1951).

(14) Weiss, M W, Hoffman, Eric and Lee, Samuel, "Copper in Textiles to be Rubberized", *Am Dyestuff Reptr* 40, 41 (1951).

(15) Millson, H E, "Sequestering Agents in Wool Dyeing", Second Canadian Textile Seminar, Supplement 94-107 (1950).

(16) Newland, Stewart H, "Application of Chlorine in the Control of Microbiological Organisms in Process Waters", *Am Dyestuff Reptr* 41, P392 (1952).

(17) Race, E, Rowe, F M, Speakman, J B and Vickerstaff, T J, *J Soc Dyers Colourists* 54, 141 (1938).

(18) Von Bergen, Werner, "Dyeing Properties of Wool Exposed to Sunlight", *Textilber* 7, 451 (1926).

TABLE XIII (Continued)

DEVELOPED DYES—EFFECT ON SHADE

2 ppm aluminum Developed		2 ppm copper Direct		2 ppm copper Developed		2 ppm iron Direct		2 ppm iron Developed	
No agent	+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1	No agent	+1% Agent #1
SH	SH	W & D	SH	similar	similar	VSW & VSD	VSW & VSD	similar	similar
VSY	similar	SW & SD	VS Br	SH & VSD	VSD	VSD	similar	SW & SD	SW
S Br	S Br	VSY & VSD	VSY & SH	similar	similar	VSH	SH	similar	similar
similar	similar	SW & VSD	SH	SW	SW	SH	SH	similar	VSB
similar	similar	SB & D	similar	SB & SD	similar	SH	SH	similar	VSB
SH & SY	SH & SY	MB & D	SW	SB & SD	SH & SY	SW	SW	similar	similar
VSY	SY & VS Br	B & D	Y & Br	B & D	SY & S Br	SW	W	similar	SW
S Br	W	MW & D	SW	W & B	W & B	SW	W	W & B	SW & B
VSR & VSD	similar	VSR & VSD	similar	VSR & VSD	similar	VSR & VSD	similar	similar	similar
SH & SR	similar	similar	similar	similar	similar	similar	similar	similar	similar
similar	similar	similar	VSR & VS Br	similar	similar	similar	VSR & VS Br	similar	similar
SB & SD	VSD	similar	SR & VS Br	similar	similar	SR & VSD	SR & VSD	similar	similar
similar	similar	SR & SD	SH	SR & VSD	SR & VSD	SD	VSH & SD	VSD	VSD
similar	similar	similar	VSH	SR & SD	VSH	VSH & VSR	VSH & VSR	similar	similar
SR	VS Br	SR & SW	VSR	SR & SD	VSR	VSR & VSD	VSR & VSD	VSR & VSD	VSR & VSD

EXPLANATION OF ABBREVIATIONS USED IN TABLES VIII THROUGH XIII

Comparisons Made to Standard

similar	=	similar
br	=	brighter
VSD	=	very slightly duller
SD	=	slightly duller
D	=	duller
MD	=	much duller
W	=	weaker
H	=	heavier
B	=	bluer
G	=	greener
R	=	redder
Y	=	yellower

APPENDIX

Methods of application used to produce dyeings are listed in Tables VIII to XIII. These methods were also used for all dyeings made during this study and modified as indicated.

Method No. 1 Liquor Ratio 60/1

Acid Dye Procedure
1% Calcocid dye
10% anhydrous Glauber's salt
3% sulfuric acid conc
Boil 1 hour.

Starting pH	2.2	Ending pH	3.1
Starting pH + 1% Agent #1	2.3	Ending pH + 1% Agent #1	3.2

Method No. 2 Liquor Ratio 60/1

Acid Dye Procedure
1% Calcocid dye
10% anhydrous Glauber's salt
3% formic acid 85%
Boil 1 hour.

Starting pH	2.9	Ending pH	3.8
Starting pH + 1% Agent #1	3.1	Ending pH + 1% Agent #1	3.9

Method No. 3 Liquor Ratio 60/1

Acid Dye Procedure
1% Calcocid dye
10% anhydrous Glauber's salt
3% acetic acid 28%
Boil 1 hour

Starting pH	3.95	Ending pH	5.3
Starting pH + 1% Agent #1	4.4	Ending pH + 1% Agent #1	5.5

Method No. 4 Liquor Ratio 60/1

Milling Dye Procedure
1% Calcocid milling dye
10% anhydrous Glauber's salt
8% ammonium sulfate
Boil 30 minutes, Add:
1% acetic acid 28%
Boil 30 minutes

Starting pH	6.15	Ending pH	5.15
Starting pH + 1% Agent #1	7.1	Ending pH + 1% Agent #1	5.25

Method No. 5 Liquor Ratio 60/1

Milling Dye Procedure
1% Calcocid milling dye
10% anhydrous Glauber's salt
8% ammonium sulfate
¼% bichromate
Boil 30 minutes, add:
1% acetic acid 28%
Boil 30 minutes

Starting pH	5.9	Ending pH	5.25
Starting pH + 1% Agent #1	7.5	Ending pH + 1% Agent #1	5.5

Method No. 6 Liquor Ratio 60/1

Metallized Dye Procedure
2% Calcofast wool dye
8% sulfuric acid
Boil 1½ hours

Starting pH	1.75	Ending pH	2.05
Starting pH + 1% Agent #1	1.8	Ending pH + 1% Agent #1	2.05

Method No. 7 Liquor Ratio 60/1

Top Chrome Procedure
2% Calcochrome dye
10% anhydrous Glauber's salt
8% ammonium sulfate
Thirty minutes to boil
Boil 30 minutes, add:
3% acetic acid 28%
Boil 30 minutes, add:
1% bichromate
Boil 30 minutes

Starting pH	6.1	Ending pH	5.3
Starting pH + 2% Agent #1	6.3	Ending pH + 2% Agent #1	5.7

Method No. 8 Liquor Ratio 40/1

Direct Dye Procedure
1% Calcodur or Calcomine dye
20% anhydrous Glauber's salt
Boil 1 hour
Cool back 15 minutes, rinse

Starting pH	5.95	Ending pH	6.45
Range	to 8.90	Range	to 8.85
Starting pH + 1% Agent #1	9.15	Ending pH range + 1% Agent #1	8.7 to 9.20

Method No. 9 Liquor Ratio 40/1

Developed Dye Procedure
1% Calcomine diazo dye
20% anhydrous Glauber's salt
Boil 1 hour
Cool back 15 minutes, rinse

Starting pH	6.0	Ending pH	6.5
Range	to 9.0	Range	to 9.0
Starting pH + 1% Agent #1	9.2	Ending pH Range + 1% Agent #1	8.7 to 9.30

Diazotizing Bath

3% sodium nitrite
5% sulfuric acid
Run cold for 20 minutes,
Rinse thoroughly

Developing Bath

A. 1.0% Developer Z
0.5% soda ash
B. 1.0% betanaphthol
0.5% caustic soda
C. 1.0% Developer MTD
0.5% soda ash
Run cold for 10 minutes
Raise slowly to 110°F
Run 20 minutes
Rinse thoroughly with warm water
Rinse in a fresh bath at 120°F

AATCC CALENDAR

COUNCIL

Apr 20 (Benjamin Franklin Hotel, Philadelphia, Pa); June 15; week of Sept 10th (New York, N Y); Nov 16; Jan 18, 1957.

NATIONAL CONVENTIONS

Sept 13-15, 1956 (Waldorf-Astoria, New York) (as part of the Perkin Centennial, Sept 10-15); 1957 (Boston); 1958 (Chicago); 1959 (Washington, DC)

HUDSON-MOHAWK SECTION

March 16 (Hotel Johnstown, Johnstown, N Y); May 18 (Ladies Nite); June 22 (Annual Outing).

MID-WEST SECTION

Feb 11 (Bismarck Hotel, Chicago, Ill); May 5 (Plankington Hotel, Milwaukee, Wis); June 16 (Outing—Browns Lake Resort, Burlington, Wis)

NEW YORK SECTION

Mar 2 (Hotel Delmonico, New York, N Y); Mar 23, Apr 27, May 18 (Kohler's Swiss Chalet, Rochelle Park, N J).

NIAGARA FRONTIER SECTION

Mar 3 (Canada—meeting to be held in conjunction with Ontario Section, CATCC); Apr 27 (U S).

NORTHERN NEW ENGLAND SECTION

Feb 17 (U S Quartermaster Research & Development Command, Natick, Mass); Apr 27 (Lowell Technological Institute, Lowell, Mass); Sept 28 (Annual Outing —Wachusett Country Club, West Boylston, Mass); Oct 19 (Science Park, Boston, Mass); Dec 1 (Annual Meeting—Hotel Vendome, Boston)

PACIFIC SOUTHWEST SECTION

Feb 6 (Gourmet Restaurant, Beverly Hills, Calif).

PHILADELPHIA SECTION

Mar 2 (Adelphia Hotel, Philadelphia); Apr 20 (Benjamin Franklin Hotel, Philadelphia); May 18 (Annual Outing)

PIEDMONT SECTION

Feb 4 (Poinsett Hotel, Greenville, S C); Apr 7 (Sir Walter Raleigh Hotel, Raleigh, N C); June 8-9 (Outing — Mayview Manor Blowing Rock, N C); Oct 6 (Annual Meeting—Hotel Charlotte, Charlotte, N C)

RHODE ISLAND SECTION

Feb 23 (Johnson's Hummock's Grille, Providence); Mar 22 (Crown Hotel and Providence Engineering Society); Apr 26 (Student Night, Rhode Island School of Design); May 25 (Ladies' Night, Sheraton-Biltmore Hotel); June 15 (Annual Outing, Pawtucket Country Club); Oct 18 (Johnson's Hummock's Grille); Dec 6 (Annual Meeting, Johnson's Hummock's Grille)

SOUTHEASTERN SECTION

Feb 18 (Auburn and Pepperell, Ala).

WASHINGTON SECTION

Feb 9 (National Housing Center, Washington, D C)

WESTERN NEW ENGLAND SECTION

Mar 16 (Rapp's Restaurant, Shelton, Conn); May 11 (Ladies' Night—Waverly Inn, Cheshire, Conn); June 15 (Outing); Oct 5 (Annual Meeting—Hartford, Conn); Nov 16 (Rapp's Restaurant, Shelton, Conn)

Color Association Announces "Perkin Centennial" Colors

IN COMMEMORATION of the discovery of the first synthetic dye by Sir William Henry Perkin in 1856, The Color Association of the United States, Inc has issued an attractive brochure highlighting three mauve shades.

In addition to the original Perkin Mauve shade, two lighter tones in the same scale, Perkin Orchid and Perkin Lilac, are also featured in the brochure. Estelle M Tennis, executive director of the Association (formerly The Textile Color Card Association of the United States, Inc), explained that these three tones were suggestive of some of the shades that could be produced, with mauve as the keynote, ranging from pastel to dark, according to the dictates of fashion.

The Color Association of the United States, Inc is among the twenty-seven leading organizations and government departments concerned with the production or application of color in the field of industry and science, which are participating in the Perkin Centennial, under the sponsorship of the American Association of Textile Chemists and Colorists. During the Perkin Centennial celebration scheduled for the week of September 10th at New York's Waldorf-Astoria Hotel, the Color Association will sponsor the topic, "Color Harmony from Fashion to Industry."

It is hoped, Miss Tennis said, that this appealing palette of three mauve tones will serve as an inspiration to all the fashion trades during the Centennial year. In addition to the Color Association's members, the brochure is also being widely issued to the trade and fashion press here and abroad, as well as to many segments of industry, trade associations, chemical and other technical societies, and the like. The AATCC is also distributing the brochure to the various participating societies and to other organizations here and overseas.

Miss Tennis believes that, during the Centennial year, wide-spread interest will be stimulated in the fashion and industrial world in the promotion of the mauve palette, because of the far-reaching significance of Perkin's discovery. It ended, she said, man's dependence on a limited number of natural dyes obtained from the earth, plants, insects and sea life and laid the foundation for our great modern dyestuff industry. The several thousand synthetic dyes now available, she added, bring a richer, more beautiful and more colorful world within the reach of everybody.

ACTIVITIES OF THE LOCAL SECTIONS

PIEDMONT

THE first meeting of 1956 of the Piedmont Section will be held at the Poinsett Hotel, Greenville, S C, on Feb 4.

W E Rixon, secretary, has announced the following program:

10:00 am———Research Committee meeting. Chairman L B Arnold, Jr, Elon College, presiding.

12:30 pm———Officers Luncheon and quarterly business meeting. Chairman Clarence Hooper, Burlington Decorative Fabrics Associates, presiding.

2:00 pm———Technical Session. Speakers: George F Jones, supervisor for textiles and special products, Research Laboratory, Imperial Paper & Color Corp, Glens Falls, N Y, "Pigments for Textiles"; and Charles R Williams, Plastics Div, Monsanto Chemical Co, Springfield, Mass, "A Study of 'Wash and Wear' Cottons." Edward A Murray, research consultant, who is in complete charge of the arrangements for the Winter Meeting, will preside over the Technical Session.

5:30 pm———Social hour.

6:30 pm———Banquet, Chairman Hooper, presiding. Henry A Rutherford, head, Dept of Textile Chemistry, North Carolina State College, will discuss his recent trip to Lima, Peru, where a new textile school is being set up. Mr Rutherford will supplement his address with illustrations.

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WASHINGTON

The Washington Section will meet Thursday, Feb 9, at 8:15 pm in the auditorium of the newly opened National Housing Center, 1625 L Street, NW, Washington, D C.

Arnold M Sookne, Harris Research Laboratories, will serve as moderator of a Symposium on "New Textile Competitors." Featured speakers will be Robert Hobbs, chief, Paper Section, National Bureau of Standards; and George A Fowles, director, Chemicals and Rubber Div, Business and Defense Services Administration, U S Dept of Commerce.

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News of the Trade

• Solvay's New H_2O_2 Installation in Operation

A new plant, new process, and new line of production are involved in the recent announcement by Solvay Process Division, Allied Chemical & Dye Corporation, that its hydrogen peroxide installation at Syracuse, N Y, under construction for the past eighteen months, has gone into operation.

The new plant, which occupies an 8-acre plot, comprises a number of buildings for the various operations involved, including synthesis, distillation and purification, packing, loading and shipping, as well as a large outdoor storage tank farm. Other facilities include the plant office as well as a wash and locker building.

Solvay's hydrogen peroxide will be produced in both 35% and 50% grades and will be shipped in aluminum drums and tank cars.

The recently completed plant is using a process initiated by Allied Chemical's Central Research Laboratory at Morristown, N J, and perfected through operation of a prototype pilot plant at Solvay's research and development center in Syracuse.

In contrast with the older electrolytic method of producing hydrogen peroxide, Solvay's process involves a chemical oxidation reaction. Hydrogen requirements for the new operation are supplied by Solvay's chlorine plant located on the adjoining tract.

Long a manufacturer of chlorine, Solvay now offers a completely rounded line of products for various bleaching purposes.

• "Chemistry of Natural and Synthetic Fibers"

Following completion of a course covering the engineering of textile structures, the Polytechnic Institute of Brooklyn is offering the second course in the textile sequence, entitled "Chemistry of Natural and Synthetic Fibers," during the 1956 spring semester.

Gerald Oster, associate professor of polymer chemistry, will present the spring course, which will deal with cotton, rayon, wool, silk and the principal synthetic fibers. It will cover the following topics dealing with the physico-chemical properties of fibers: morphology, birefringence, x-ray diffraction, chemical constitution and interchain force, molecular weight, water sorption and swelling, interactions with dyes, viscoelastic behavior with relation to molecular structure, and optics.

• Union Carbide Forms Silicones Division

Silicones Division, Union Carbide and Carbon Corporation, has been formed to take over the responsibility for the development, manufacture, and sale of silicone products.

The new Division will assume responsibilities in the field of silicones previously handled by Linde Air Products Company. Silicones which have been marketed under the "Linde" trade-mark, will now be called "Union Carbide" silicones.

William B Humes, whose previous assignment was as vice-president of Union Carbide Canada Limited, has been appointed president of the new Division. T J Coleman, formerly general manager of the Linde Silicones Department was named general manager of the new Division.

Capacity of the new silicone plant at Long Reach, W Va, on the Ohio River between Parkersburg and Wheeling, will be enlarged early in 1956. Expenditure of an additional $1,000,000 for expansion of the operation to increase the reactor capacity and install additional equipment for compounding silicone rubbers is planned, it is reported.

Production at the existing smaller silicone plant at Tonawanda, N Y, will also continue.

• J-M Looking to Increased Asbestos Textile Sales

An accelerated research program and increased production of Johns-Manville asbestos textiles will mean greater service and satisfaction for the company's customers in 1956, according to Edward A Schuman, manager of Johns-Manville's Asbestos Textile Department.

Mr Schuman also cited the recent split of the Johns-Manville Industrial Products Division into three new operating divisions as a move which would improve service to customers for J-M asbestos textile products.

"The Asbestos Textile Department is now part of the J-M Packings and Friction Materials Division, which plans to concentrate more facilities in upgrading the quality of the textiles manufactured," Mr Schuman said.

Mr Schuman, who will head the company's drive for increased sales of asbestos textiles, joined Johns-Manville in 1952. He had been associated with American Cyanamid Company as a chemist for nine years prior to that time.

• SOCMA Creates New Award

The Synthetic Organic Chemical Manufacturers Association, through its president, R W Hooker, has announced the creation of an annual award for Creative Work in Synthetic Organic Chemistry. The award will be administered by the American Chemical Society.

The first of its type, this award has been created "to recognize and encourage creative work in synthetic organic chemistry," and consists of $1,000, a certificate, and a gold medal. Suitable traveling expenses for receipt of the award will be furnished the recipient.

The rules of eligibility state that the award is to be made "for creative work in synthetic organic chemistry published in an American journal during the preceding three years ending January 1 of the year in which the selection is made." It will be presented for the first time in 1957.

"Creative work in synthetic organic chemistry" is defined as that which will "stress creative concepts and theories which apply to synthetic organic chemistry as well as actual synthetical methods."

The SOCMA Research Committee which created the plan for this award is comprised of Ernest M May, Otto B May, Inc, chairman; Alvin H Tenney, Carbide and Carbon Chemicals Company; and August Merz, American Cyanamid Company.

• Cravenette Names New Sponger Agent

The Cravenette Company, USA, Eighth and Madison Streets, Hoboken, N J, has announced the appointment as an authorized sponger agent of Stanley H Goldsmith, Inc, 22nd and Lehigh, Philadelphia, Pa.

In this capacity, Stanley H Goldsmith, Inc, will be authorized to apply "Cravenette" Super Silicone finishes to a wide range of woolen and blended fabrics.

• 11th Purdue Industrial Waste Conference

Approximately fifty papers dealing with industrial wastes and their treatment will be presented at the 11th Purdue Industrial Waste Conference, scheduled for May 15-17 in the Purdue Memorial Union, Purdue University, Lafayette, Ind.

Hotel reservations can be made at the Purdue Union Club, Fowler Hotel, Cedar Crest Hotel, and Morris Bryant Hotel.

Registration blanks may be obtained by writing to Don E Bloodgood, professor of sanitary engineering, School of Civil Engineering, Purdue Univ, Lafayette, Ind.

NAMES IN THE NEWS

Klein

Hustwit

Krashin

Rimlinger

SAMUEL KLEIN, 65, prominent in the dyestuffs field for over fifty years, retired January 1 from his post of manager of the Mid-Western Territory for American Cyanamid Company. Mr Klein, however, will continue his association with Cyanamid as a consultant.

This association goes back to 1906, when he joined A Klipstein & Company, a predecessor company. He joined Cyanamid's Organic Chemicals Division in 1917 and has remained with that division in the dyestuffs field ever since.

Starting as a general salesman, Mr Klein became manager of the former Lake Department in 1920, working closely with dyestuffs manufacturers, dry color makers and jobbers on sales of dyestuffs. In 1944, he was transferred to Chicago to head sales of dyestuffs and textile resins.

Taking over the Chicago Office, located at 3505 N Kimball Avenue, is E I STEARNS, who has been assistant manager for the past year.

ARTHUR HUSTWIT, for the past year assistant plant manager of Bradford Dyeing Association (USA), has joined Soluol Chemical Co, Inc, Natick, R I.

Mr Hustwit, who began working with Bradford in 1924 as a laboratory assistant, and for the 16 years prior to becoming assistant plant manager was superintendent of dyeing with that concern, will serve as director, technical sales in his new capacity at Soluol.

HERBERT B WOODMAN, president of Interchemical Corporation, has again consented to be chairman of the Chemicals Division of The Legal Aid Society's fund-raising campaign for 1956. This will be Mr Woodman's ninth consecutive year serving the Society in this capacity. Assisting him as co-chairmen will be LAWRENCE A COLEMAN, Allied Chemical and Dye Corporation; ROBERT C PORTER, Charles Pfizer & Company; and GEORGE EDWARD COTTER, Freeport Sulphur Company.

BERNARD R KRASHIN has been appointed president of the Colton Chemical Company division of Air Reduction Company, Inc, succeeding H SEYMOUR COLTON, who resigned to devote his time to personal affairs.

Mr Krashin has been the vice president in charge of sales of the Colton Chemical division. He was one of the organizers and has been in charge of the sales of the Colton Chemical Company, Cleveland, Ohio, since its inception in 1943. The business and properties of the Colton Chemical Company were acquired by Air Reduction in June, 1954.

Headquarters of the Colton Chemical division will be maintained in Cleveland.

ALFRED P RIMLINGER has been named export manager of the Antara Chemicals Division, General Aniline & Film Corporation. He succeeds PAUL F HAND, who was recently appointed assistant to the president of GAF.

Mr Rimlinger has been assistant export manager for dyestuffs since 1942 and previously served as import manager. He first joined General Aniline in 1936.

JAMES BALLOCH, Southern representative of Jacques Wolf and Co for the past three years, will shortly join Ivey Chemical Co, Inc, Greenville, S C, as sales manager.

Ivey Chemical will distribute a complete line of industrial chemicals, and will offer technical service and warehouse distribution.

EDWARD ARTIM, formerly director of laboratories at S Augstein & Co, Inc, has joined the research laboratory staff of J C Penney Co.

Mr Artim has been active in AATCC's Committee on Dimensional Changes in Textile Fabrics, having served as chairman of the Knitted Woolens Division during 1955.

Especialização

— PORTUGUESE FOR

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IN ANY LANGUAGE,

PEERLESS MEANS SPECIALIZATION

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521-535 North Avenue, Plainfield, New Jersey

Manufacturers of Dye Colors since 1916.

Export Representative: Herbert Lorenz, Inc., World Traders

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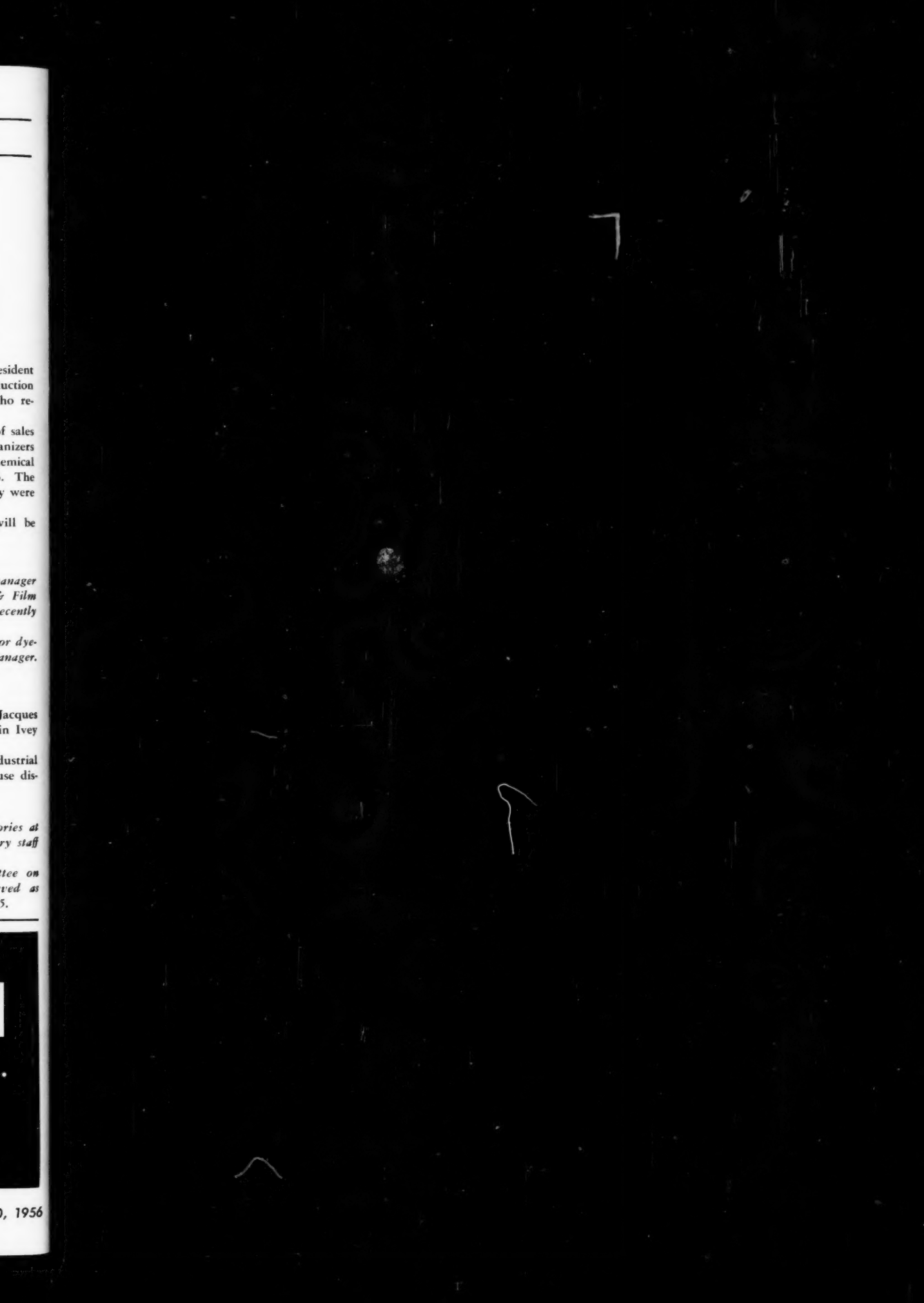
Cables: HACOLORENZ